CONTAMINATED SITE REMEDIATION: FROM SOURCE ZONES TO ECOSYSTEMS

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Volume 1

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From Source Zones to Ecosystems

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C.D. Johnston

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2000

Contaminated Site Remediation Conference

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Preface

The 2000 Contaminated Site Remediation Conference is the second in a series presented in Australia by the Centre for Groundwater Studies and follows on from the very successful 1999 conference held in Fremantle Western Australia. Our continued vision for the 2000 conference was to bring together within Australia the gamut of society involved in contaminated site remediation issues – regulators, researchers, technologists, consultants and industry – and to balance their technological, economic and societal concerns. Contaminated site remediation continues to be a rapidly evolving field and the conferences have provided the opportunity to consolidate and share experiences within Australia as well as review trends occurring internationally.

The organising committee for the 2000 conference was keen not only to focus on remediation techniques but also to consider contaminated site remediation in the overall context of risks to the environment and human health as well as the preservation of ecosystems. For this, an overall theme of "From Source Zones to Ecosystems" was adopted for the conference. The theme recognised that once released into the environment, contaminants followed a pathway from the source zone to the point of impact with an ecosystem or other receptor. This raises several salient issues on what exactly are the effects of the contaminants on ecosystems and other receptors, how are the risks determined and what targets need to be set, where and how is it best to intervene to reduce the risks and how is it best to investigate and monitor the risk and any remediation efforts. To focus on these issues, the conference was divided into four sub-themes:

(a) Remediation to Reduce Impacts to Ecosystems – How Do We Set Targets?
(b) Investigation and Monitoring of Remediation and Ecosystems – Beyond National Protocols
(c) Levels of Intervention to Manage Environmental Risk – Does Monitored Natural Attenuation Have a Role in the Remediation Tool Kit?
(d) Remediating Complex Source Zones – What's Really Achievable?

The papers presented here - the proceeding of the conference - provide a guide to the current practice and future direction of contaminated site remediation in Australia and internationally. Several important issues can be gleaned from the contributed papers. There is an increasingly acute awareness of the effect of contaminants on ecosystems and other receptors. Consequently, there are greater efforts to associate remediation with reducing risk to these receptors. Monitored natural attenuation is also receiving much attention and there is an increasing body of evidence available to evaluate this approach to managing site contamination for Australian conditions, compared to other techniques. Source zones, particularly where nonaqueous phase liquid organic contaminants are present, continue to be problematic. There is keen investigation and debate on how remediation in these instances may be achieved and the extent to which attempts at removing the contaminant source reduces the risk to the environment. Interestingly, remediation strategies for heavy metal contamination continue to appear to be underdeveloped and indeed underrepresented given the recognised extent of the problem. While phytoremediation is being developed to ameliorate the problem, there is also a focus on the bioavailability of the metals and on better defining the risk they pose.

Many have contributed to the 2000 Contaminated Site Remediation Conference and the proceedings presented here are only part of the material outcomes. Our thanks to the organising committee who embraced the vision for the conference, the sponsors of the conference, the keynote speakers for sharing their valuable experience and all our other international and Australian colleagues and co-workers for sharing their perspectives from Australia and beyond.

Greg Davis and Colin Johnston
Centre for Groundwater Studies
CSIRO Land and Water

Table of Contents

Volume 1

Investigation and Monitoring of Remediation and Ecosystems – Beyond National Protocols

Volume 2

The Logic of Ecological Risk Assessment for Contaminated Sites

G.W. Suter II

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ABSTRACT: Risk assessment provides technical support for choosing remedial actions at contaminated sites. It is necessary that risk assessments address risks to nonhuman populations and communities because they are usually more exposed than humans and some are likely to be more sensitive. Because of the expense of remedial actions, it is important to perform reliable assessments. Because of the potential complexity of ecological risk assessments, it is necessary to perform them in an efficient manner. At minimum, three distinct phases of assessment should be used. A scoping assessment defines the problem using existing, often qualitative, information. A screening assessment narrows the scope to a set of contaminants of concern and end point receptors. A definitive assessment provides risk estimates and other pertinent information to the risk manager and stakeholders. Following the remediation, additional assessments may be performed to determine the adequacy of the remedial action. Each of these assessments has its own logic, determined by the types of information that are available and the decisions to be made.

KEYWORDS: ecological risk assessment, remediation, screening, remedial goals, weight of evidence

INTRODUCTION

Ecological risk assessment (ERA) provides essential support for remedial actions at contaminated sites by identifying risks to nonhuman populations and communities due to no action and active remedial alternatives. It is particularly important to assess ecological risks at contaminated sites for two reasons. First, nonhuman organisms are more at risk than humans, because they are more immersed in the site. They often live out their lives on a site, obtain all of their food and water from the site, and engage in activities that make them highly exposed, such as drinking from sumps or respiring contaminated water. In addition, nonhuman organisms are more affected by remedial actions. Removing vegetation and soil, dredging, and other remedial actions kill organisms and destroy habitats.

Various regulatory agencies and remedial authorities have developed or are developing guidance and procedures for these ERAs. However, there appears to be a common underlying logic for this process. That logical process, as presented in this paper, is shown diagrammatically in Fig. 1. Appropriate methods for each stage are discussed briefly here and at length in Suter *et al.* (2000).

SITE CHARACTERISATION AND SCOPING

The first step is to gain a basic understanding of the nature and extent of site contamination, potential routes of exposure and ecological resources present on the site. This requires a site and reconnaissance survey and accumulation of existing information from literature, files, and interviews. Data collected during the preliminary site characterisation should be used to perform a scoping assessment, which will serve as the ecological risk

assessor's input to the problem formulation. The purpose of a scoping assessment is to determine whether the site poses a hazard that may be worthy of additional assessment.

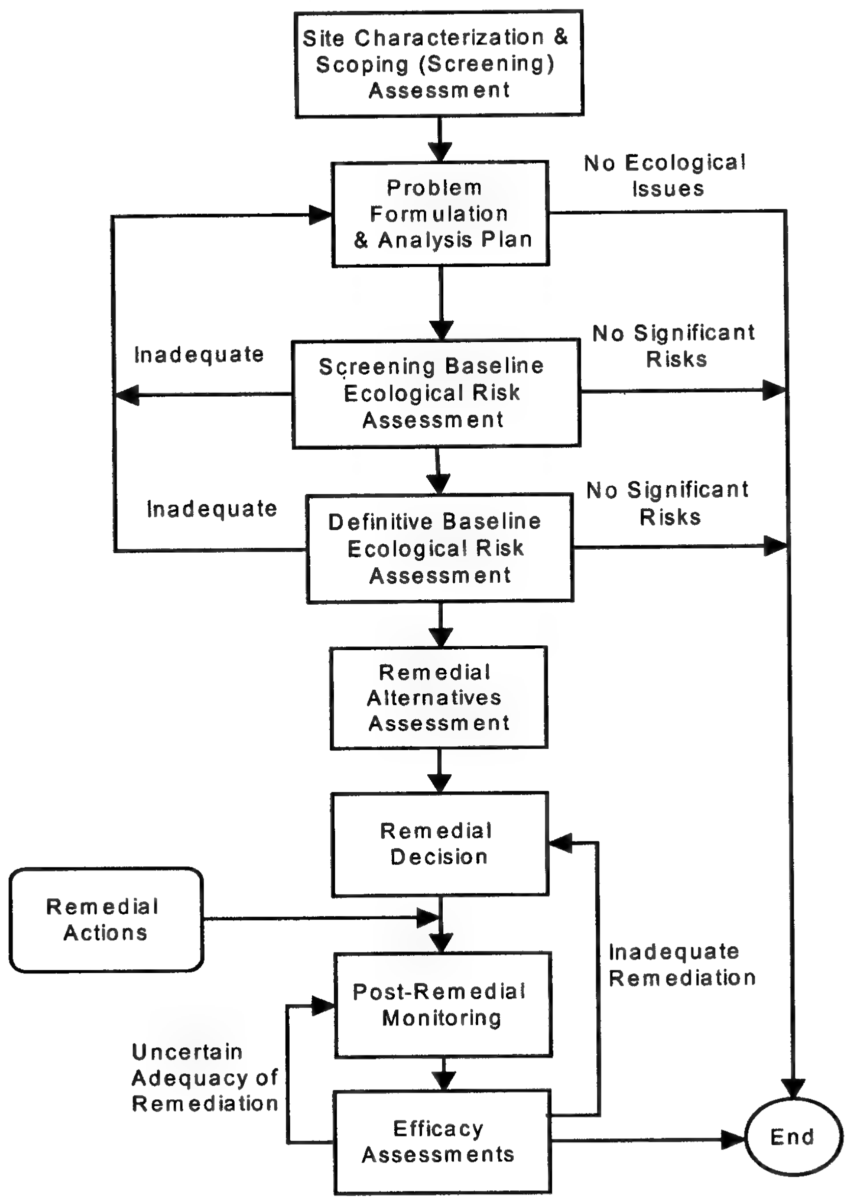

Fig. 1. Diagram of a generic process of risk assessment and remediation of contaminated sites.

The site characterisation should include:

(a) a map of the site and vicinity showing sources of contamination, known contaminated areas, features that could provide routes of transport, biotic communities, and other relevant features;
(b) a preliminary conceptual model of the means by which sources could induce effects including routes of transport and exposure, processes that could induce secondary effects, and potential end point receptors;
(c) a summary of existing data concerning the site;
(d) a summary of the results of the site reconnaissance; and
(e) a narrative description of the assessors' judgements concerning the site.

In addition, in those rare cases where a sufficient body of data exists, a screening assessment should be conducted, as discussed below.

PROBLEM FORMULATION AND ANALYSIS PLAN

The problem formulation defines the purpose, scope and methods of the assessment. Its output includes the assessment end points, the conceptual model, and the analysis plan. The problem formulation should be performed as a collaboration between the assessors and the decision maker. The decision maker is the ultimate judge of what will be a useful assessment. However, the decision maker is seldom as familiar with the site as the assessors or as knowledgeable concerning environmental chemistry or ecology. The degree and form of participation of the decision maker and of stakeholders, such as land owners and community representatives, vary widely among nations and even sites.

Defining assessment end points is often difficult. These end points are ecological entities (e.g., a fish community) and associated properties (e.g., number of species) that are of sufficient importance to potentially prompt a remedial action. They should be societally valued, susceptible to the contaminant exposure, have an appropriate scale for the site, and, ideally, be significant components of the ecosystem (Suter 1989, USEPA 1992). The difficulty arises primarily from the interpretation of broad policy goals such as ecological integrity in terms of a limited number of operationally definable end points.

The conceptual model should be developed in conjunction with the identification of end points. It defines the assessment by identifying the sources that may be removed, the media that may be remediated, the end points to be assessed, and the processes that link them. These are usually flow charts with explanatory text.

The final product of the problem formulation is the analysis plan. That plan defines the sampling, testing and analysis to be performed and the data analyses and assessment models to be applied. The plan must assure that the data will be of sufficient quantity and quality to support the assessment, and that the data analyses and models will provide adequate estimates of the end points. In many cases, the assessment will be performed in stages. Preliminary sampling, testing and analysis can provide the basis for a screening assessment that will reduce the scope of subsequent studies. In addition, preliminary studies provide better estimates of variance and effort to help design definitive studies.

SCREENING BASELINE ASSESSMENT

Baseline assessments address current risks in order to determine whether the no-action alternative is appropriate. They include screening and definitive baseline assessments. Screening baseline assessments determine the scope of subsequent assessments by eliminating from further consideration chemicals and receptors that are clearly not associated with potentially significant risks. Chemicals may be screened out if (a) they are not detected and analytical methods are acceptable, (b) the concentrations are within background ranges, or (c) the concentrations are so low as to not pose a toxic hazard. Although screening is conceptually straight-forward, it may present difficult problems in practice. For example, are regional background concentrations adequate, or must local background be used? How many samples are sufficient to assure that a chemical is absent or occurs at low concentrations? Might storm events or other episodic exposures be missed? Does the species of a chemical in the waste differ from that in background?

Of the screening criteria, the determination of the potential toxic hazard is the most difficult to evaluate. The trick is to make the assessment sufficiently conservative to ensure that no hazardous chemicals are excluded without being so conservative that many

nonhazardous chemicals are included. On the exposure side, this means using the maximum observed concentration or a high percentile of the distribution of concentrations. Other conservative assumptions include restriction of the hypothetical receptor to consuming the most contaminated food items, drinking only wastewater and completing its life cycle on the site. On the effects side this means using ecotoxicological benchmarks that correspond, as far as possible, to sensitive responses in sensitive species. When available data are inadequate, safety factors may be employed to ensure sufficient conservatism.

Although screening assessments are primarily devoted to eliminating individual chemicals, they may also eliminate media and receptors. That is, if all chemicals in a medium are nonhazardous, taking into consideration combined effects, the medium may be eliminated from further assessment. Similarly, if all chemicals or media to which an end point receptor is exposed are eliminated, that receptor is eliminated.

DEFINITIVE BASELINE ASSESSMENTS

Definitive assessments support remedial decisions by estimating the likelihood of end point effects. Because only the chemicals and receptors not excluded by the screening assessments are addressed, focused studies may generate multiple lines of evidence. ERAs differ from health risk assessments in this regard. Health risk assessments are nearly always limited to the comparison of modelled exposures to toxicological benchmark values. In contrast, ecological risk assessments may employ biological surveys, toxicity tests of contaminated media, and, like health risk assessments, laboratory single chemical toxicology.

Biological surveys involve counting or measuring some property of an exposed biological population or community for comparison to survey results from reference sites. Biological surveys are often conducted for fish and benthic invertebrate communities of contaminated streams. They are less commonly employed for terrestrial communities or for large water bodies because the techniques are less accurate and precise. Interpretation of biological survey data is difficult for two reasons. First, many factors may influence the abundance, production, tumor frequency, or other property of populations and communities. Second, it may be difficult to identify a relevant and reliable reference condition. Use of an upstream site or other single reference site provides no appropriate estimate of variance and is likely to be confounded by extraneous factors such as difference in flow, channel morphology, or soil compaction. Nevertheless, biological surveys are potentially important because they provide estimates of the true biological response. These difficulties can be minimised by designing biological surveys to reveal gradients, rather than to make binary comparisons of contaminated and reference sites. This can allow the assessor to model the relationships among the biological measures, contaminant levels, and habitat properties.

Toxicity tests may be performed on contaminated media or on the waste itself. In the U.S. short-term chronic tests that were originally developed for regulation of aqueous effluents are commonly used at contaminated sites. Additional tests have been developed for sediments and soils. These tests have many advantages as assessment tools because they provide much more control of causation than biological surveys and much more realism than traditional single chemical tests. Tests of contaminated media ensure appropriate consideration of combined toxic effects, bioavailability, chemical form, chemicals that have not been individually tested, and background levels of the contaminants. Obtaining these benefits requires some care in the collection and handling of media and in the selection of reference media. As with biological surveys, it is best to design testing programs to identify relationships between the response and both levels of contamination and important properties of the media. Examples of the latter include the organic matter content of sediments and the pH of waters.

Single species toxicity tests and measurements of chemical concentrations in site media provide the most common line of inference in contaminated site risk assessments. The toxicity data are usually obtained from the literature, and may be either individual test end points such as LC_{50}s or derived benchmarks such as water quality criteria. In contrast, the exposure concentrations are from site media, so they may represent different forms of the chemicals and media as well as different averaging times. The most common form of risk characterisation for this line of evidence is the hazard quotient, which is simply the quotient of the ambient exposure concentration divided by the toxicologically effective concentration. More sophisticated assessments use exposure-response distributions and distributions of exposure over time or space. Combined toxic effects may be estimated by assuming a mode of joint toxicity, most commonly concentration or dose addition.

If only one line of evidence is used, risk characterisation is relatively straight forward. If multiple lines of evidence are available, one has the opportunity to generate a more reliable risk characterisation, but the process is more complex and more open to controversy. A characterisation based on an analysis of the weight of evidence may be derived by literally weighting each piece of evidence based on its presumed reliability and importance (Menzie *et al.* 1996). While the consistency of such as system is advantageous, a logical process is potentially more powerful. A logical weighing of evidence can elucidate the consistencies among lines of evidence and explain the inconsistencies in a way that provides a more defensible risk characterisation. Biological surveys are highly realistic but are poorly controlled and often highly variable. Media toxicity tests are better controlled and isolate toxicity from other stressors, but may not be representative of site species or exposures. Single chemical toxicity tests can indicate which chemicals are responsible for toxic effects and elucidate modes of action, but provide the least realistic estimates of effects. Table 1 presents an example summary of a simple weight of evidence analysis.

COMPARISON OF REMEDIAL ALTERNATIVES

A baseline risk characterisation determines whether significant effects on the assessment end point are occurring, but it does not determine what, if anything, should be done. A remedial decision may be reached by setting preliminary remedial goals, assessing the consequences of alternative means of achieving those goals, and devising a remedial plan.

Preliminary Remedial Goals

The design of remedial alternatives requires design goals. The process begins with the list of the ecological end points that are currently unacceptably injured, or would be in the future. Preliminary remedial goals (PRGs) must be established for each. The most common form of PRGs is a concentration in a medium that should not be exceeded. That concentration may be a regulatory criterion or a risk-based value. This approach is complicated by the fact that toxic effects are often a result of the combined toxicity of a mixture. Therefore, it may be necessary to assume some model of joint toxicity. Alternatively, one may define PRGs in terms of toxicity, that is, one may require remediation of any soil or sediment that is toxic in a particular test. Similarly, one may require remediation of a toxic spring, leaking sump or other source. Finally, one may set a PRG that requires restoration of communities that are found to be degraded based on biological surveys.

Table 1. A table summarising the risk characterisation for the species richness and abundance of a fish community in a stream at a waste site (Suter *et al.* 2000)

Evidence	Result[a]	Weight[b]	Explanation
Biological Surveys	-	H	Fish community productivity and species richness are both high, relative to reference reaches. Data are abundant and of high quality
Ambient Toxicity Tests	±	M	High lethality to fathead minnow larvae was observed in a single test, but variability is too high for statistical significance. No other aqueous toxicity was observed in 10 tests.
Water Analyses/Single Chemical Tests	+	M	Only Zn is believed to be potentially toxic in water and only to highly sensitive species.
Weight-of-Evidence	-		Reach 2 supports a clearly high quality fish community. Other evidence which suggests toxic risks is much weaker (single chemical toxicology) or inconsistent and weak (ambient toxicity tests).

[a] Results of the risk characterisation for each line of evidence and for the weight of evidence,
\+ indicates that the evidence is consistent with the occurrence of the end point effect.
\- indicates that the evidence is inconsistent with the occurrence of the end point effect.
± indicates that the evidence is too ambiguous to interpret.
[b] Weights assigned to individual lines of evidence: High (H), Moderate (M), and Low (L).

Remedial Alternatives Assessment

Remedial alternatives range from no action (let degradation and dilution remediate the site) to severe options such as removal of all vegetation and surface soil. The assessment of alternatives is often dominated by engineers who attempt to identify the solution that meets the remedial goals at least cost. However, the comparison of alternatives is complicated by the fact that remediation may release contaminants (e.g., by re-suspension of sediments), create new contaminants (e.g., in incinerator effluents), and cause physical damage to the environment, as well as human injury or death. Therefore, it is necessary to balance the human and ecological risks and benefits of remedial alternatives (Suter *et al.* 1995). Balancing risks may be relatively straightforward if human and ecological risks are similar and if remediation need not be environmentally damaging. However, if the choice is difficult, it will be necessary for the assessors to provide good descriptions of the nature and magnitude of effects, and associated uncertainties. For the ecological assessor, this may require deciding whether one line of evidence provides the best risk estimates, or whether a risk model must be generated that includes input from multiple lines of evidence.

The design of remedial alternatives is complicated by the selection of PRGs based on toxicity of biological attributes rather than chemical concentrations. Toxicity-based PRGs would require a sampling and testing design that would identify sources and extent of toxicity. However, this need not be more expensive than equivalent chemical analyses. However, if the remediation involves treatment rather than removal, prototype treatments may be needed to ensure that toxicity is actually eliminated. If the PRGs are defined in terms of biological attributes, it is necessary to consider remedial alternatives beyond the removal of contaminants. Unimpaired biotic communities are achieved by restoring the habitat as well as removing contaminants. The population or community attributes to be achieved should be derived from the assessment end points. Other considerations may be included such as the site's context, whether urban, rural, or natural. However, given the damage done to the site by

a responsible party, it is not unreasonable to expect it to be restored to an exemplary condition.

MONITORING AND EFFICACY ASSESSMENT

In most cases, the contaminants will not be completely removed or destroyed and the site will not be completely restored. In such cases, it is important to monitor the site to determine whether the end point properties will recover as expected. Biological surveys can provide a better measure of risk reduction than contaminant monitoring. In the U.S. monitoring is conducted for five years, at which time an assessment of remedial efficacy is performed. If the system has not recovered, additional monitoring and assessment may be required. If the system is not improving properly, additional remediation or restoration may be required.

CONCLUSIONS

The types and intensities of ecological studies at contaminated sites will depend on the size of the site, its potential ecological value, and the ecological value of adjoining areas that may become contaminated. However, in all cases the assessment should be organised and conducted in a logically defensible manner. While a generic logic such as that presented here is useful at all sites, it is important to make the ecological risk assessment and the supporting studies appropriate and relevant to the site rather than being generic or pro forma. Often, a few site-specific ecological studies are more revealing of ecological risks and less expensive than a cookbook program of sampling and analysing contaminated media. They must, however, be based on a clear agreement among the parties concerning what should be protected and what estimates of risks to those end points will be considered adequate.

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The New ANZECC and ARMCANZ Water Quality Guidelines and Their Application

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ABSTRACT: The new ANZECC and ARMCANZ (2000) Australian and New Zealand water quality guidelines incorporate a number of innovations. These include a risk-based approach to move the user away from compliance based on single numbers to more holistic evaluations. The new guideline trigger values have been calculated from laboratory ecotoxicity data using a statistical-distribution scheme, which derives a figure to protect a given percentage of species, usually 95%. The Guidelines encourage site-specific assessment using a risk-based decision scheme that takes into account water quality parameters that may modify toxicity of the chemical, and hence the site-specific guideline, or its bioavailable concentration at the site. The scheme emphasises direct toxicity assessment using an appropriate suite of aquatic organisms and test endpoints to further assess risk. Consistent schemes for derivation and use have highlighted knowledge gaps and research needs to facilitate future revisions.

KEYWORDS: water quality guidelines, toxic contaminants, risk, biological assessment

INTRODUCTION

Land and aquatic systems are integrally linked; therefore there is always a potential for contaminants to migrate from contaminated land into water. Where this occurs, numerical ambient guidelines for toxicants in receiving waters are an essential tool for water management. In Australia and New Zealand, managers of contaminated sites have been using the ANZECC (1992) guidelines. Since 1996, these have been undergoing an extensive revision process, which was finalised in 2000. The new revised ANZECC and ARMCANZ (2000) Australian and New Zealand *Guidelines for Fresh and Marine Water Quality* incorporate a number of innovations, which can improve the effectiveness of the assessment of contaminated sites. A new risk-based approach to water quality management aims to move the user away from compliance based on single guideline numbers to more holistic evaluations.

This paper discusses the revised water quality guidelines for chemical contaminants (termed "toxicants"), with emphasis on how they relate to contaminated sites. The guidelines can be applied with different emphases to different conditions of ecosystems. Three levels of ecosystem protection are suggested: ecosystems with *high conservation* or ecological value; *slightly - moderately disturbed* systems; and *highly disturbed* systems. It is intended that a consultative process will result in a decision regarding the classification of an ecosystem of interest. The management aim should be to continually improve those systems that are *highly disturbed* and to protect, if not improve, the remainder.

DERIVING GUIDELINE TRIGGER VALUES FOR TOXICANTS

The Guidelines provide a framework for setting environmental limits for a range of commonly encountered chemicals, based on available data on environmental effects. Extrapolating from laboratory ecotoxicity data to effects in the field (OECD 1992) involves uncertainties and value judgements. All guideline values for individual chemicals are, at best, estimates of maximum concentrations that are unlikely to cause adverse environmental effects.

As most interpretable concentration-response data are from single-species laboratory toxicity tests, trigger values were calculated from such data on a range of test species (OECD 1992). The previous guidelines (ANZECC 1992) were derived by dividing the lowest acute or chronic toxicity figure by an arbitrary safety factor, called an "assessment factor". The revised guidelines provide trigger values that have been calculated using a risk-based statistical distribution method designed to protect a given percentage of species (e.g. Table 1). The trigger values are given at one of three levels of reliability, depending on the data available: *high reliability* from field or chronic data; *moderate reliability* from acute data; and *low reliability* from an insufficient data set. Reliable (*high* or *moderate reliability*) trigger values were derived for 83 chemicals in freshwater and 28 in marine waters, using a risk-based statistical distribution method, outlined below. *Low reliability* trigger values for over 125 additional chemicals have been derived using the old assessment factor method, where there were insufficient data for the statistical method ("ID" in Table 1). They can be used as indicative interim working levels for preliminary decisions until suitable data can be obtained.

The statistical distribution methods are based on a probability distribution of effects from a range of toxicity data (OECD 1995), which is assumed to represent the spread of sensitivities in the field. A recent CSIRO method (Campbell *et al.* 2000) was used to fit the distributions to a wide range of curves. This approach estimates a pre-determined level of protection, usually 95% (Warne 1998). Higher protection levels (99%) were used for chemicals that had the potential to bioaccumulate or when figures derived from chronic toxicity data failed to protect significant test species from acute toxicity and vice versa. They may also be used as default values, in the absence of biological data, for ecosystems with *high conservation* value. Lower protection levels (e.g. 90%) may be used for *highly disturbed* ecosystems, provided the lower protection level is not likely to cause acute toxicity.

For some chemicals, the main issue of concern is not the direct toxic effects but the indirect risks associated with bioconcentration, bioaccumulation and biomagnification. There is no formal and specific international guidance on incorporating bioaccumulation into water quality guidelines (Bro-Rasmussen *et al.* 1994). Hence these trigger values have not attempted to take secondary poisoning into consideration, except to recommend 99% protection levels in the interim for those chemicals likely to be in this category (see Table 1). Users may further consider bioaccumulation in the decision scheme for applying the guidelines. If suitable data are available, there are equations for estimating water concentrations to protect from bioaccumulation but developing *tissue residue guidelines* (CCME 1997) may be a more robust approach.

During the process of deriving the guidelines, it was quickly recognised that no data sets for any two chemicals are the same and it was necessary to establish ground rules for acceptance of data on the basis of type and quality. In addition, the statistical models have minimum requirements for numbers of data points; at least 5 data points from at least 4 different taxonomic groups (Warne 1998). There were other requirements, such as use of ecologically-relevant endpoints and the necessity for hardness data to be supplied with metal toxicity figures (Warne 1998). Metal trigger values are reported at low hardness of 30 mg L^{-1}

$CaCO_3$, under which conditions toxicity should be highest. The trigger values are usually calculated using data from laboratory tests that maximise the bioavailability of the chemical.

Table 1. Examples of trigger values (TVs) (μg L^{-1}) for toxicants at alternative levels of protection (from ANZECC & ARMCANZ 2000). Values in grey shading are the trigger values applying to typical *slightly–moderately disturbed systems.*

Chemical		TVs for freshwater (μg L^{-1})			TVs for marine water(μg L^{-1})		
		Level of protection (% species)			Level of protection (% species)		
		99%	95%	90%	99%	95%	90%
INORGANIC CHEMICALS							
Ammonia	D	310	900 ^{C}	1450 ^{C}	490	910	1200
Arsenic (As III)		1	24	94 ^{C}	ID	ID	ID
Cadmium	H	0.06	0.2	0.4	0.7 ^{B}	5.5 ^{C}	14 ^{C}
Cyanide	F	4	7	11	2	4	7
Lead	H	1.0	3.4	5.6	2.2	4.4	6.6 ^{C}
Mercury (inorganic)	B	0.06	0.6	1.9 ^{C}	0.1	0.4 ^{C}	0.7 ^{C}
Zinc	H	2.4	8.0 ^{C}	15 ^{C}	7	15 ^{C}	23 ^{C}
INDUSTRIAL ORGANIC CHEMICALS							
Aniline		8	250 ^{A}	1100 ^{A}	ID	ID	ID
Aroclor 1254 – PCB	B	0.01	0.03	0.07	ID	ID	ID
Benzene		600	950	1300	500 ^{C}	700 ^{C}	900 ^{C}
Dibutylphthalate	B	26	37	45	ID	ID	ID
Naphthalene		2.5	16	37	50 ^{C}	70 ^{C}	90 ^{C}
Phenol		85	320	600	130	270	390
Pentachlorophenol		7.5	12	17	11	22	33
1,2,4-trichlorobenzene	B	55	95	120	20	80	140
1,1,2-trichloroethane		5400	6500	7300	140	1900	5800 ^{C}
PESTICIDES & HERBICIDES							
DDT	B	0.006	0.01	0.02	ID	ID	ID
Endosulfan	B	0.03	0.2 ^{A}	0.6 ^{A}	0.005	0.01	0.02
Chlorpyrifos	B	0.00004	0.01	0.11 ^{A}	$2x10^{-8}$	0.0002	0.01
Diazinon		0.00003	0.01	0.16 ^{A}	ID	ID	ID
Atrazine		0.7	13	45 ^{C}	ID	ID	ID
Trifluralin	B	2.6	4.4	6	ID	ID	ID

A = Figure may not protect key test species from acute toxicity. (trigger value ≥ acute toxicity figure); B = Chemicals for which bioaccumulation effects should be considered ; C = Figure may not protect key test species from chronic toxicity ; D = Ammonia as TOTAL ammonia as [NH_3 – N] at pH 8. ; F = Cyanide as un-ionised HCN, measured as [CN]; H= Chemicals for which algorithms have been provided to account for the effects of hardness. The values have been calculated using a hardness of 30 mg L^{-1} $CaCO_3$.; ID = Insufficient data to derive a reliable trigger value (i.e. *low reliability* value).

APPLICATION OF THE GUIDELINES TO SPECIFIC SITES

The revised Guidelines provide an optional stepwise risk-based decision scheme to guide users in taking site-specific parameters into account i.e. determine how they modify the overall toxicity or bioavailability of the specific toxicants. Hence the guideline figures (Table 1) are termed "trigger values", because they are intended to trigger some action. The steps either provide a more accurate estimate of the bioavailable concentration of the toxicant at the site, for comparison with the trigger value, or calculate a site-specific guideline value that takes into account changes in toxicity at the site. The factors that are considered in the outline of the stepwise approach are listed in Table 2. Each step enables the user to consider whether the particular chemical poses a low, intermediate or high risk at the site. The ultimate step in

the scheme is direct toxicity assessment using an appropriate range of species and chronic endpoints to determine if toxicity is actually occurring.

Table 2. Optional[1] steps in applying the risk-based decision scheme for toxicants

	Suggested Action	Notes and Caveats
Ecosystem condition	*High Conservation*: No detectable change in biodiversity	Apply 99% as default if no biodiversity data
	Slightly-moderately disturbed: 95% protection	99% for some (eg bioaccumulators)
	Highly disturbed: First 95% then 90% or lower	Check bioaccumulation and acute toxicity
Sampling	First measure "totals"	Guidance given to consider many issues
Analytical PQL[2]	If PQL >TV, any reliable detection implies WQG exceeded	PQL should not become *de facto* trigger value
Background levels	If reliable background conc'n > TV, 80th percentile becomes WQG	
Transient exposure	Very little data.	Possible kinetic modelling (Delos 1994)
Bioaccumulation	If data available, use equations in Guideline text	OR calculate *tissue residue guidelines* (CCME 1997)
Local species important	Obtain additional ecotoxicity data on this species and recalculate	Original data in CD-Rom
Water quality/Chemical factors		
– Formulation	Apply factors if known	e.g. Some herbicides
– Suspended matter	Apply factors if known	
– DOM[3]	Apply factors if known	
– Salinity	Apply factors if known	
– pH	Apply factors if known.	For metals – see "hardness"
– Temperature	Apply factors if known	OR examine original data and adjust
– Hardness	Algorithms for metals	
– Speciation	Modelling, Chemical analysis	Check with toxicity test
– Other	Eg. DO, Cyanide forms	
Simple mixtures	Apply TTM equation – see text	e.g. BTEX. Go to DTA if complex
Direct Toxicity Assessment (DTA)	At least 3 spp from different trophic levels – preferably 5	Van Dam & Chapman (in press)

Table notes: 1. The scheme is optional in that, at any stage, one can accept the guideline value and institute managerial action; 2. PQL = Practical Quantitation Limit often ea. 5 times higher than method detection limit; 3. DOM = Dissolved Organic Matter; TV = Trigger Value;

The first step in the site-specific assessment is to decide on the ecosystem category, and hence the appropriate level of protection arising from the environmental values of the ecosystem. One then proceeds through the decision scheme (Table 2), measuring those water quality parameters that are most likely to affect toxicity and applying mathematical relationships, where available, between the parameter and the chemical toxicity. If it is cost-effective, each chemical may be initially measured as total concentration in an unfiltered sample for comparison with the guideline trigger value. If the total concentration is below the trigger level, there is usually no need to proceed further. In many cases, particularly for organic chemicals, quantitative relationships will not be available but it will sometimes be possible to indicate whether chemical risk will be increased or decreased at the site.

Where the site-specific guideline for a toxicant is exceeded, management action will normally result. In practice, not all site-specific data on a particular chemical are equivalent in extent, detail or method. If a manager were to apply the strict requirements used in deriving the original guideline trigger value, much valuable local information would be lost. Differing

site-specific trigger values developed using various methods can be examined and weighted according to predetermined criteria of quality and relevance to the ecosystem. This should be done in a commonsense manner consistent with principles of risk assessment commonly applied by managers of contaminated sites to arrive at an appropriate figure (e.g. Menzie *et al.* 1996). Inclusion of these multiple lines of evidence strengthens the overall result by integrating varying types of information on a particular site.

If the ambient concentration is above the site-specific guideline value or if the chemical is one of a complex mixture of chemicals, a *Direct Toxicity Assessment (DTA)* (van Dam and Chapman in press) may be undertaken.

APPLICATION OF THE GUIDELINES IN SPECIFIC CIRCUMSTANCES

Caution in Reducing the Level of Protection: Endosulfan

The statistical distribution method provides a lower level of protection (Table 1), which catchment managers may apply to *highly disturbed* ecosystems, subject to approvals and consultation. It is important however that modified values for lower levels of protection do not approach concentrations that may cause acute toxicity. For example the 95% protection figures for endosulfan (0.2 $\mu g\ L^{-1}$) and aniline (250 $\mu g\ L^{-1}$) exceed acute toxicity levels for some key species, including Australian fish. This usually arises when trigger values that have been calculated from chronic toxicity do not account for acute toxicity or vice versa.

Incorporating pH: Phenol and Ammonia

The effect of pH on metal toxicity is at least partially considered in the hardness algorithms (see below). Changes in pH can also alter the toxicity of a few organic chemicals, such as phenols. The only organic chemical for which pH algorithms have been reported is pentachlorophenol (USEPA 1986). The trigger value for PCP is 7.5 $\mu g\ L^{-1}$ (99% protection). The 4-d USEPA algorithm gave equivalent guideline values of 1.8, 7.5 and 24 $\mu g\ L^{-1}$ at pH 6.5, 7.8 and 9.0 respectively. There are no similar algorithms for phenol but literature data suggested an increase in the toxicity of phenol to fish with decreasing pH (ANZECC and ARMCANZ 2000). On this basis, the phenol freshwater trigger value of 320 $\mu g\ L^{-1}$ would reduce to around 60-100 $\mu g\ L^{-1}$ at pH 4.6 and increase to 500-800 $\mu g\ L^{-1}$ at pH 8.8.

The toxicity of *ammonia* is affected by pH, due to the equilibrium between free ammonia and ammonium ion. Trigger values were calculated by converting all acceptable chronic NOEC data, reported at different pH values, to total ammonia at a common pH value of 8.0 before applying the statistical distribution derivation method. The Guidelines provide tables for trigger values at different pH levels and for inter-conversion of free and total ammonia. For instance, the trigger value for total ammonia is 900 $\mu g\ L^{-1}$ at pH 8.0 (where un-ionised ammonia comprises 3.8% of total at 20°C). However, at pH 6.5, the value is 2490 $\mu g\ L^{-1}$ and at pH 9.0 it is 180 $\mu g\ L^{-1}$ (un-ionised ammonia comprises 0.1% and 28% respectively of total at 20°C).

Incorporating Water Hardness and Chemical Speciation: Metals

Increasing water hardness (calcium and/or magnesium concentration) reduces the uptake and toxicity of several metals, including cadmium, chromium (III), copper, lead, nickel and zinc, to freshwater organisms. The relationship between water hardness (H: expressed in mg

L^{-1} as $CaCO_3$) and toxicity of these six metals is best described using an algorithm, as below, to derive a "hardness-modified trigger value" (HMTV) from the original trigger value (TV):

$$HMTV = TV\ (H/30)^a$$

where a is a constant. The algorithms may be used at any water hardness but are most reliable between 25 and 400 mg L^{-1} as $CaCO_3$.

The following hypothetical case of copper in a river system illustrates the procedure: An initial measurement of total copper in an unfiltered water sample of 14.5 µg L^{-1} is higher than the TV for copper of 1.4 µg L^{-1}. The water hardness was moderate (90 mg L^{-1} of $CaCO_3$) and an HMTV of 3.6 µg L^{-1} was derived. The sample was filtered through a 0.45 µm filter, acidified and dissolved copper was measured at 6.4 µg L^{-1}, still above the HMTV. Speciation modelling showed that dissolved inorganic copper was 1.8 µg L^{-1} and chemical measurements of labile copper using anodic stripping voltammetry gave a similar figure (2.0 µg L^{-1}). This was confirmed when the sample was shown to be non-toxic to sensitive algal species. Hence, the bioavailable copper was below the modified trigger value, and the water quality was considered acceptable.

Batley (2000) cites an example illustrating the cost effectiveness of this approach, which saved a major water authority from the need to spend several million dollars to improve their treatment process to remove a metal whose concentration exceeded the guideline for the dissolved fraction. A study of its speciation, costing several thousand dollars, showed that the bioavailable fraction of the metal was considerably below the guideline value, and this was accepted by the regulatory authority.

Incorporating Toxicant Mixtures

No chemical-specific guidelines, including ANZECC and ARMCANZ (2000), consider the possibility of toxicity interactions between chemicals. Warne (1998) suggests a theoretical method for accounting for the toxicity of simple mixtures, using the following total toxicity of the mixture (TTM) formula:

$$TTM = \Sigma(Ci\ /\ WQGi)$$

where Ci is the concentration of the i'th component in the mixture and WQGi is the guideline for that component. If TTM exceeds 1, the mixture has exceeded the water quality guideline. Further, if the aqueous concentration of *any* chemical in the mixture exceeds its guideline figure, then the water quality guidelines are automatically exceeded. For the commonly encountered mixture BTEX, it is necessary to work with a mixture of *moderate* and *low reliability* trigger values: benzene 950 µg L^{-1}; toluene 180 µg L^{-1}; ethylbenzene 80 µg L^{-1}; *o*-xylene 350 µg L^{-1}; *m*-xylene 50 µg L^{-1}; *p*-xylene 200 µg L^{-1}. If a hypothetical mixture contained the following concentrations, respectively 300, 100, 50, 200, 20 and 100 µg L^{-1}, each individual chemical is below the corresponding trigger value. However, the TTM is almost 3, and the mixture exceeds the guidelines.

Incorporating Direct Toxicity Assessment (DTA)

Direct toxicity assessment (DTA) of effluent or ambient water, either in the laboratory or *in situ* in the field, is the best method to integrate the toxicity of mixtures and to determine whether adverse effects on biota may occur. Methods and protocols are currently available for testing a number of Australian and New Zealand species. It is anticipated that DTA would

only be employed in cases where there is a complex mixture of chemicals entering the specific waterbody and where either the resultant toxicity cannot be easily estimated or the prediction needs to be checked.

The main considerations in establishing a test program using DTA are selection of test species and dilution water, the nature of pollutant(s), test methods and statistical analysis. Effects are determined at a range of concentrations of effluent or contaminated ambient waters, diluted with local reference waters, to allow calculation of a concentration-response curve. From this, a LOEC, NOEC and EC/LC50 (with 95% confidence limits) value are calculated. Normally a safety factor may be applied to a NOEC or EC50 value, in line with the guideline derivation procedure (eg. divide by 10 for NOEC and 100 for acute EC/LC50) but there may be an argument for treating the data in some other way.

Toxicity identification and evaluation (TIE) procedures, using concurrent chemical separations and toxicity tests, enable identification of the classes of contaminants resulting in the observed toxicity, and hence effective targeting of effluent treatment actions. Some recent studies in Australia have successfully applied TIE to sewage treatment plant effluents, to minimise toxicity in receiving waters (Bailey *et al.* 2000). The Guidelines also place considerable emphasis on field biological assessments, where appropriate, and provide detailed guidance on undertaking such assessments.

CONCLUSIONS

The innovations incorporated in the new ANZECC and ARMCANZ (2000) Guidelines can improve the overall effectiveness of the assessment of contaminated sites, particularly the site-specific assessment using the risk-based decision scheme to account for water quality and other parameters that may modify toxicity. In addition, if earlier steps in the decision scheme indicate probable risk or if mixtures of several chemicals are involved, the user may undertake direct toxicity assessment using an appropriate suite of aquatic organisms and test endpoints to further assess the risk. These tools allow a redefinition of the risk associated with contaminants on site and allows for a more comprehensive assessment of the significant risk of harm.

The derivation process has highlighted a number of data gaps. There is a need to incorporate bioaccumulation into guideline derivation and application. There are also data gaps on specific chemicals, particularly details of how the water quality parameters at specific sites may affect toxicity. An improved understanding of the interaction of contaminated groundwaters with ambient waters will assist managers of contaminated sites to apply the guidelines.

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Ecological Risk Assessment at Contaminated Sites in New Zealand

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ABSTRACT: A government-funded programme was initiated in late 1997 to develop a decision support system (DSS) to assist risk managers in making informed ecological risk assessments at contaminated sites, and examine New Zealand-specific environmental tolerance levels for key contaminants in soils at contaminated sites in New Zealand. The programme involved the determination of the most suitable risk assessment models, software and guidance documents, characterisation of mobility of the key contaminants in New Zealand soils and aquifers, and the development of standardised toxicity testing protocols for a range of representative New Zealand species inhabiting both terrestrial and aquatic environments. These components were integrated within an internet-based DSS, to maximise functionality and accessibility for the target end-users. A series of workshops and meetings provided a forum to publicise the DSS and seek feedback from end-users.

KEYWORDS: ecological risk assessment, contaminated sites, standardised toxicity tests, decision support system

INTRODUCTION

Contaminated sites are the legacy of chemical manufacture, use and disposal. Preliminary studies indicate contaminated land is relatively common in New Zealand – an estimate of over 7200 contaminated sites (excluding approximately 600 timber treatment sites, and 1000 farm sheep and cattle dips) has been made for New Zealand. These sites can pose hazards to both human health and ecosystems.

Environmental risk managers, including risk assessors, environmental scientists and toxicologists are increasingly required to assess the risk posed by contaminated land to both human health and ecosystems. These assessments are likely to include the potential for both human health and ecological effects under a variety of different land uses.

Human health risk assessment methodologies, based on sector industries are relatively well established in New Zealand, whereas methods for assessment of ecological effects are in the early stages of development. Efforts are being made to develop a more consistent approach to ecological risk assessment for contaminated sites in New Zealand, based on recent advances in overseas ecological risk assessment methods and decision support systems.

Improved management of contaminated sites in New Zealand requires a uniform

standard and ecotoxicological-based approach for dealing with heavy metals, pesticides and the volatile components of gasoline at contaminated sites.

A Foundation for Research, Science and Technology (FRST) funded programme, entitled "Environmental Tolerances in Contaminated Sites", was initiated in late 1997. The purpose of this programme is to develop tools which will assist risk managers to make informed ecological risk assessments at contaminated sites and derive New Zealand-specific environmental tolerance levels in soil, groundwater and surface water for key contaminants.

Progress toward this goal has been achieved through a multi-disciplinary effort involving Landcare Research, Geochemical Solutions, NIWA, Lincoln Environmental and Tonkin & Taylor, focussing on the following areas:

(a) a comprehensive review of internationally available risk assessment methods and software;
(b) identification of New Zealand-specific requirements and knowledge gaps;
(c) measurement of the relative mobilities of contaminants in New Zealand sub-soils;
(d) assessment of appropriate ecotoxicological assays for New Zealand soil fauna and flora, aquatic invertebrates and native fish, and the development of protocols for testing contaminant effects on these species under New Zealand conditions;
(e) development of a decision support system (DSS) integrating risk assessment models, contaminant mobility models, and tolerance levels for ecological receptors to assist end-users in the assessment and management of contaminated sites.

The programme aims to develop an internet-based DSS, and examine the toxicological effects of a suite of heavy metals, including copper, chromium and arsenic, and volatile organics consisting of benzene, toluene, ethylbenzene and xylene (BTEX) in soils at contaminated sites in New Zealand. The programme involves the determination of suitable risk assessment models and software, characterisation of contaminant mobility in New Zealand soils and aquifers, and the identification and development of ecotoxicological tests and procedures that will provide locally generated data to be integrated into the DSS.

ECOLOGICAL RISK ASSESSMENT

Ecological Risk Assessment (ERA) is a procedure designed to identify hazards and to determine the risks to the natural environment. The basic components of an ecological risk assessment are presented in Fig. 1 (NEPC 1999).

The ecological risk assessment process consists of an initiation phase, followed by problem identification, receptor characterisation, exposure assessment, toxicity assessment and risk characterisation. The DSS describes each of these components and the required tasks, including relevant information sources, documents, databases and models that may be appropriate for use. Ecological risk assessment is more complicated than human health risk assessment due to:

(a) the large number organisms and the complexity of relationships existing within ecosystems, introducing uncertainty and ignorance surrounding the structures, components and processes of ecosystems;
(b) a lack of a clear or direct link between some environmental effects and causes;
(c) the difficulty in determining effect levels on receptors; and
(d) long time spans as ecological change may emerge slowly, due to delay between cause and effect.

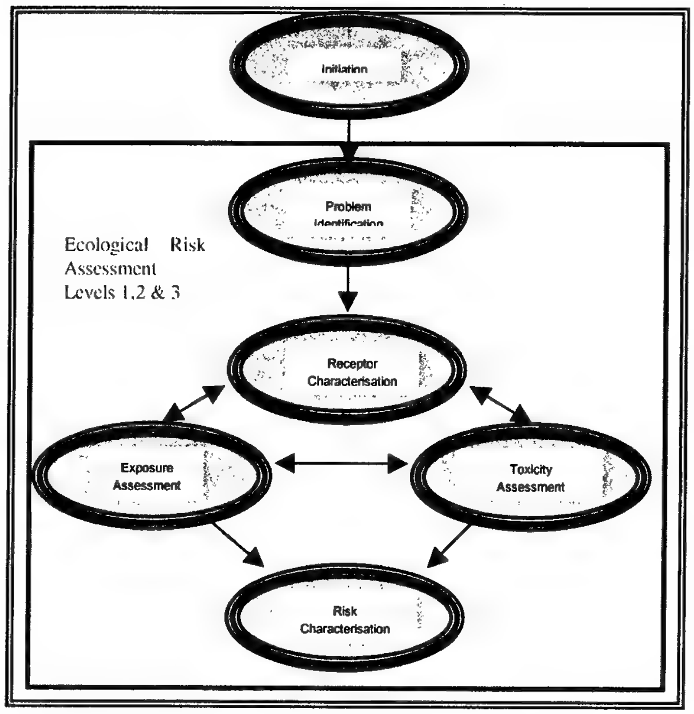

Fig. 1. Components of an ecological risk assessment (adapted from NEPC 1999)

REVIEW OF RISK ASSESSMENT MODELS AND GUIDANCE DOCUMENTS

An initial review of internationally available risk assessment methods and software has been completed. Over 600 reports and publications, including internet databases and approximately 70 risk assessment and contaminant migration and dispersion computer models have been reviewed for their suitability within the DSS. The focus of the review was on the advantages and disadvantages of suitable models, and how readily they can be applied within the DSS.

This review investigated the ability of each candidate model to provide guidance to investigators on site characterisation, and on the identification and evaluation of multiple pathways and receptors. Other review criteria included the suitability of the model (in terms of the New Zealand environment and regulatory setting) for incorporation into a NZ-based DSS, and the ability of the model to incorporate new ecotoxicological values as they were generated. Furthermore, the ability of the model to assess human health as well as ecological risks was also evaluated. The results of this evaluation have been incorporated into an accessible database on the website.

During the evaluation process, it became clear that many ecological risk assessment models are at present either in the development or beta testing stage (for example *AQUARISK*, developed by Australian Nuclear Science and Technology Organisation). Few models met the dual criteria for basic ease of use and the ability to undertake comprehensive assessments.

The review focussed on the applicability of multimedia fate models to simulate contaminant transport and transformations within multiple environmental media, and, more recently, specifically on the ability of comprehensive ecological risk assessment models to simulate and predict the ecological effects of contaminants in soil and water ecosystems. The most common types of ecological risk assessment models consist of a combination of environmental fate, food-web bioaccumulation, and toxicological sub-component models.

In the last several years, a substantial volume of ERA guidance documents and methodologies have been developed, principally by the USEPA, and agencies in the Netherlands, Canada, the European Union, and Australia. Currently, the assessment and management of contaminated sites in New Zealand and Australia has been generally consistent with the *Australian and New Zealand Guidelines for the Assessment and Management of Contaminated Sites* (ANZECC/NHMRC 1992). In addition, a series of industry-based guidelines have been developed and are widely applied in New Zealand (MfE, 1997, MfE/MoH 1997, MfE 1999).

These guidelines recognised, however, the need to further develop aspects of contaminated site assessment and management. The methodology described in the Guideline on Ecological Risk Assessment, developed as part of the National Environment Protection (Assessment of Site Contamination) Measure (NEPC 1999), may also have application in New Zealand.

TRANSPORT OF HEAVY METALS AND BTEX IN NEW ZEALAND SOILS AND AQUIFERS

The relative retention of heavy metals (arsenic, cadmium, chromium, copper, lead, nickel, mercury and zinc) and BTEX (benzene, toluene, ethylbenzene and xylene) has been measured in a number of characteristic or significant New Zealand subsoils. Small batch experiments were used to measure the distributions of the metals and BTEX between water and the soil, and distribution coefficient (K_d) values were determined from these. In particular, the results showed that the soil type had little effect on the BTEX concentration in the water solution, with the exception of the peat soil, which removed most of the species from solution.

This information has been incorporated in a spreadsheet-based system for determining relative mobilities of the metals and BTEX in water from contaminated sites. The calculations use soil-, site- and climate-specific factors and weights them to derive descriptions of the potential for the contaminants to reach groundwater and downstream aquatic environments.

The system is based loosely on the DRASTIC parameters (i.e. Depth to Groundwater, Recharge, Aquifer Media, Soil Media, Topography, Impact of the Vadose Zone, Hydraulic Conductivity), but is extended by including such factors as rainfall, time since emplacement, quantity, and distance to receiving waters. These factors were weighted and multiplied together, rather than added as in the DRASTIC system. Logical conflicts and options were catered for in the spreadsheet calculations. The system has been tested using a number of case studies and will be made available on the web site. Continuous improvement of the model is envisaged as further case studies are incorporated in the DSS.

STANDARDISED ECOTOXICITY TESTS

Standardised toxicity testing protocols have been adapted and developed for a range of representative New Zealand species inhabiting both terrestrial and aquatic environments. These organisms include indigenous (or common naturalised) soil invertebrates, native and common crop plant species, native freshwater invertebrates and fish species. The selection criteria included: known contaminant sensitivity for these species groups; available laboratory methods for acute and chronic tests with related species; widespread occurrence in New Zealand and ecologically important species in their environments. The tests include seedling emergence and growth tests in three plant species, invertebrate growth and survival tests (using earthworms and woodlice), and acute (mortality) and chronic (survival and reproduction) assessments in several aquatic invertebrates and native fish.

The plant bioassays assess emergence and growth of one native New Zealand species (kaka beak *Clianthus puniceus*) as well as in two standard test species (millet *Panicum milliaceum*, and lettuce *Lactuca sativa*). The plant tests were based on an OECD procedure (OECD 1984a), but incorporated many of the recommendations outlined in an ASTM guideline (ASTM 1994). *Eisenia foetida* which is the recommended test earthworm species in international protocols (OECD 1984b) has little relevance for the New Zealand soil environment as it is largely a dung-dwelling species. Therefore, the pasture earthworm *Aporrectodea caliginosa*, which is one of the most common topsoil species in New Zealand, was selected as a test invertebrate species, thus increasing the relevance for the risk assessment of soil contaminants. Many international guidelines suggest that tests are conducted in artificial soil, but we have found that *A. caliginosa* is unable to maintain good health under these conditions. A 'natural' silt-loam soil was considered preferable as it allowed for extrapolation to field conditions, as well as being able to support the plant tests. The earthworm bioassay is a modification of the OECD guideline and runs for 28 days in order to determine the effects on growth and mortality.

The woodlouse, *Porcellio scaber*, was selected as the second invertebrate for ecotoxicity determinations. Woodlice play a critical role in organic matter decomposition and related processes that are essential to soil health and are commonly found, and abundant in, New Zealand soil litter. The woodlouse test methods are based on Hornung *et al.* (1998). The data from the terrestrial tests are presented elsewhere in these proceedings (see O'Halloran and Booth 2000). A comparison of the results with the overseas literature suggests that ecotoxicity values derived from tests using the earthworm *E. fetida* can underestimate chemical impacts on *A. caliginosa.* Our results also highlight the fact that the test media selected for these 'standardised' tests can influence the toxicity of the metal. For example, a test result for plant toxicity in an artificial soil can greatly overestimate the toxicity of a metal in natural soil. Until a relationship can be established between soil characteristics and the bioavailability, form, and subsequent toxicity of metals to soil flora and fauna, a full comprehension of the test conditions for overseas derived data is required.

Two native freshwater invertebrate species, a cladoceran and an amphipod, and two native fish species, the common bully (*Gobiomorphus cotidianus*) and the inanga (*Galaxis maculatus*) have been identified for use in acute (short-term) and chronic (long-term) toxicity testing. A literature review has been completed and large international databases have been identified for copper and chromium but very limited data for arsenic is available to facilitate comparison of the relative sensitivity of the native species. The sensitivity of the test species to individual chemicals was compared to published values for other native and overseas species and ranked to determine the relative sensitivity and for numeric guideline derivation (Fig. 2). The sensitivity of the test species are also compared to a benchmark species (e.g. rainbow trout). Acute toxicity guidelines are derived for short-term exposures (e.g., stormwater run-off events) while chronic toxicity guidelines are suitable for protection from adverse effects associated with long-term exposures. A wide range in acute sensitivity is commonly found between species (e.g. a range of approximately 1000 times for copper and 2400 times for chromium – Fig. 2), indicating considerable scope for the development of site-specific guidelines. Chromium showed a marked difference between fish and invertebrate species sensitivities indicating that site-specific guidelines could consider the different exposure risks to these groups. Both native fish species were in the upper 50-percentile of the acute and chronic toxicity datasets, indicating a relatively low susceptibility to copper or chromium exposure. The greater sensitivity of rainbow trout to copper indicates that trout would provide a useful surrogate for protection of the native species, however, the inanga was more sensitive to chromium. Amphipods and cladocerans were in the lower 30-percentile

indicating high sensitivity and the potential for these species to provide sensitive indicators for ecosystem protection. Amphipods were also found to be acutely sensitive to arsenic.

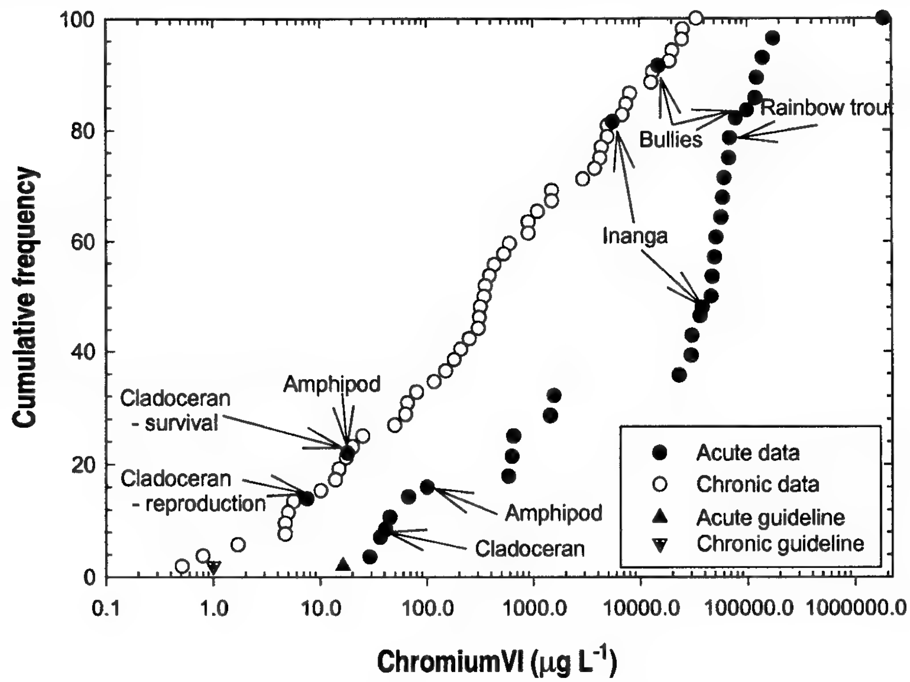

Fig. 2. Summary data for chromium in freshwater showing cumulative frequency plot of organism sensitivity for data used to derive revised ANZECC water quality guidelines (from Hickey and Pyle 2000), and showing sensitivity of native New Zealand species. Acute guideline from US EPA (1996) and chronic guideline from ANZECC/ARMCANZ (2000).

END-USER CONSULTATION

A critical component in the development of the DSS has been consultation with end-users. Early in the project regional council and Ministry for the Environment staff (ranging from scientists to policy analysts and planners) were consulted, to determine what kinds of assessments they currently undertake, the tools they used, and the types of tools that would be of assistance to them. From these early discussions a group of key contacts for each council was identified.

A workshop was held in Auckland in 1998, at which the research team presented preliminary results and discussed the nature of these results with end-users. At the same time a questionnaire was circulated to key contacts requesting feedback on the specifications and applications of the DSS, and the range of ecotoxicological tests which will become available in New Zealand through this programme. This input was used to focus the development of the DSS. The research team has continued to promote the goals and aims of the project to a range of targeted audiences through workshops, conferences and regional waste officers' forums.

With the completion of the website, a programme of communication with the identified end-users and other interested parties (such as consultants and councils) is being prepared. This will involve a regular newsletter as well as a series of visits to councils and workshops to demonstrate the use of the DSS, and to seek comment on its accessibility and utility.

INTERNET-BASED DECISION SUPPORT SYSTEM

The risk assessment models, contaminant mobility models, and tolerance levels for ecological receptors have been integrated into an internet-based DSS to assist end-users in the assessment and management of contaminated sites. The decision was made to develop the DSS on a dedicated internet website, in order to simplify access to the DSS for end-users. The website and its associated links are intended to provide a decision support system:

(a) to assist people to make decisions about whether or not to undertake an ERA on a potentially contaminated site, since not every site will require exhaustive investigation in order to develop appropriate management options; and
(b) to assist in deciding which steps to follow, and what methods to use, and depending on the characteristics of the site, the contaminants and the ecological values that require protection.

The website also provides the user with a recommended bibliography of information sources including books, reports, databases, websites and models that can be referenced for further details. The website will provide information to assist decisions regarding how to undertake each stage of an ERA, and for managing the risk at the site of concern.

The posting of the DSS on the Internet at the address below marks the conclusion of the first phase of the programme (1999/2000):

http://www.landcare.cri.nz/science/ecotox/contamsites

Future components of the programme include validation of the DSS using data from standardised toxicity tests at existing contaminated sites in collaboration with end-users, and evaluation of the functionality, performance characteristics and applicability of ERA models to 'real world' problems.

CONCLUSION

Review of internationally-available risk assessment guidance and software has demonstrated the complexity of ecological risk assessment compared to human health risk assessment, due principally to the large number of organisms and the complexity of relationships existing within ecosystems. Evaluation of the mobility of key metals and BTEX in New Zealand soils has been undertaken, and the K_d presented in spreadsheet format within the DSS. Standardised ecotoxicity testing protocols have been developed for a range of representative New Zealand species inhabiting both terrestrial and aquatic environments, and results of the tests documented in the DSS. The integration of ERA methodologies, models and New Zealand data within an internet-based DSS, has maximised functionality and accessibility for the target end-users. The DSS has been designed to provide guidance to both uninitiated and experienced risk assessors in evaluating and prioritising potential ecological risk associated with contaminated sites. A series of workshops has been used to present the DSS to end-users, and collect feedback to target future improvements and developments.

ACKNOWLEDGEMENTS

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Health Risk Assessments and their Role in Managing Environmental Risk

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ABSTRACT: Changes in community awareness and the realisation that guidelines are generic and not always applicable, are resulting in increasing emphasis being placed on managed risk whether it is related to site occupational health and safety risk, economic risk or in the case of this paper 'environmental risk'. In New Zealand, the current emphasis is on developing site-specific criteria for managing contaminated sites and this has involved the use of health risk assessment (HRAs) in many cases. Health risk assessments have also been used extensively in the USA and UK. In Australia to date, health risk assessments have not been commonly used as a tool to derive site-specific criteria for remediation or management purposes. This paper looks at the development of site remediation criteria through undertaking a HRA using site-specific data. Given the variation in background chemistry of Australian soils compared to that of countries from which many of our accepted guidelines have developed, there is a perceived need for site-specific criteria in Australia. Hence in Australia questions arise such as: should HRA's be used more often?; in conjunction with existing Australian derived health-based guidelines?; how much faith should we put in models such as RBCA or RISC for calculating site-specific 'cleanup' goals by assessing potential human health and environmental risk associated with soil, groundwater and vapour contamination at a site? and who can judge if the criteria will 'adequately' manage any environmental risk? This paper will attempt to answer these questions using case in point examples where HRA's have been used as a tool in developing remediation criteria including a case study in Australia where site-specific data is more appropriate then applying generic guidelines.

Developing Risk-based Remediation Criteria for Asbestos

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ABSTRACT: There is no generally accepted criterion for the allowable concentration of asbestos fibres in soils on residential sites. As such, a site-specific, risk-based approach has been developed for determining acceptable concentrations of asbestos fibres in soils for a large former industrial site in Sydney, proposed for residential redevelopment. This approach has incorporated determining a site specific relationship between asbestos concentration in soils and asbestos concentration in generated dust. This relationship was then applied to an estimation of lifetime dust exposure from the site to calculate lifetime asbestos fibre exposure as a function of asbestos concentration in soil. This was then solved to an acceptable level of risk to determine an acceptable level of asbestos in the soil. As developed, this procedure would be able to be replicated on other asbestos impacted sites.

KEYWORDS: risk, asbestos, contamination, remediation, air dispersion

INTRODUCTION

Egis Consulting Australia (ECA), the Asia Pacific partner of Groupe Egis, were commissioned to investigate and remediate a large former industrial site in the Sydney area, proposed to be redeveloped for a range of urban uses including residential. A large portion of the site had been found to be impacted with asbestos fibres in surface soils typically to a depth of 300 mm. No generally accepted criterion for concentration of asbestos fibres in soils on residential sites is available in Australia. Remediation of asbestos fibres has generally been required to be performed to a standard of non-detection. Remediation to this standard would have presented a prohibitive (multi-million dollar), and most likely unnecessary, cost. Thus, a site-specific, risk-based asbestos criterion has been determined for the site by ECA, under the review of a NSW EPA-accredited site auditor.

SITE DESCRIPTION

The 'site' is located in Sydney, and is approximately 50 ha in area. The site has been used for a variety of commercial and industrial purposes since the 1890s. The soils impacted by asbestos fibres comprise fine- to medium-grained sands with silt and traces of clay fines and roots. The site is vegetated primarily with a patchy grass cover.

SITE CONTAMINATION

The site was found to be contaminated with several organic and inorganic substances located at discrete hotspots across the area of the site. Remediation techniques for these substances are well understood and protocols for validating remediation of these substances are well established.

The site was also found to have widespread asbestos fibre contamination. The existence of asbestos fibre contamination was a consequence of the widespread use of asbestos cement sheeting, generally used as cladding on buildings, across the area of the site. A majority of these asbestos cement clad buildings were demolished approximately thirty years ago by bulldozing the buildings into large stockpiles. The asbestos fibre contamination on the site is believed to have been primarily caused by the breaking of asbestos cement sheets during this demolition.

HEALTH RISK POSED BY ASBESTOS FIBRES

Asbestos is the name applied to a group of six different minerals that occur naturally in the environment. These minerals are made up of long, thin fibres which are somewhat similar to fibreglass. Asbestos is neither volatile nor soluble; however small fibres may occur in suspension in air.

Asbestos fibres are a confirmed human carcinogen (USEPA Group A), based on epidemiological studies of workers exposed to high levels of asbestos. Lung effects are a major health concern, as chronic (long-term) exposure to asbestos in humans via inhalation can result in a lung disease termed asbestosis. Other effects from chronic inhalation exposure to asbestos include an accumulation of scar like tissue in the membranes that surround the lung, pulmonary hypertension, and immunological effects. Cancer is a major concern from asbestos exposure, as inhalation exposure can cause lung cancer and mesothelioma (a rare cancer of the thin membranes lining the abdominal cavity and surrounding internal organs) and possibly gastrointestinal cancers in humans.

Environmental Regulations and Guidelines

Risk-based guidelines and approaches regarding the development of soil acceptance criteria for asbestos have not been published within Australia, or by other international environmental agencies (e.g., the World Health Organisation - WHO). Similarly, generic soil criteria, such as the health-based soil investigation levels developed by the National Environmental Health Forum, are not available for asbestos. Guidelines developed for environmental auditors do not specifically address the complex issues related to asbestos exposure and toxicity. A literature review was conducted to determine if there were any published or widely accepted methods of calculating risk-based soil criteria for asbestos, but did not reveal any novel or useful approaches.

Due to the lack of any guidance or relevant precedents, it was necessary to develop a site-specific methodology for evaluating the potential human health risks posed by asbestos in soil. Well accepted risk assessment methodologies developed and recommended by the Australia and New Zealand Environment and Conservation Council (ANZECC), the WHO and the USEPA were used as the basis for developing the risk-based criteria. In addition, Australian exposure assumptions and recommendations from the Contaminated Sites Monograph series (South Australian Health Commission) were used in the risk assessment.

RISK ASSESSMENT APPROACH

In conducting a health risk assessment, the possible exposure routes of a compound are required to be first identified. The only exposure route of concern identified by studies for asbestos fibres is by chronic exposure through inhalation.

The dose-response factors used in the assessment of risk associated with inhalation exposure to a carcinogen may be defined as follows:

- Unit Risk (UR): incremental lifetime risk of cancer associated with lifetime exposure to a unit concentration (1 fibre mL^{-1}) of asbestos fibres in air. Unit risk factors are derived from the cancer slope factor for the inhalation of carcinogenic chemicals.

A unit risk value of 0.23 (fibre mL^{-1}) has been developed by the USEPA and was used as the toxicological basis of this risk assessment.

In order to estimate the incremental lifetime risk of cancer associated with exposure to carcinogenic chemicals, the results of both exposure and toxicological assessment need to be combined. For a carcinogenic compound, this risk may be calculated as follows:

$$\textbf{Risk} = \mathbf{C_{adj}} * \textbf{Unit Risk}$$

where: Risk = incremental lifetime risk of cancer
C_{adj} = adjusted asbestos fibre air concentration

In undertaking this assessment, an acceptable level of risk was defined as a risk of less than $1*10^{-6}$ incremental lifetime risk of cancer.

UNDERTAKING THE RISK ASSESSMENT

The goal of the risk assessment was to establish an acceptable concentration of asbestos fibres in soils. This was achieved by the following steps outlined below, and discussed in more detail in the remainder of the document:

(a) establishment of a relationship between asbestos fibre concentration in soils and asbestos fibre concentration in dust generated by undertaking field studies;
(b) estimation of the dust generation of the subject site for the risk assessment exposure period;
(c) calculation of lifetime dust exposure and subsequent calculation of lifetime asbestos fibre exposure of most affected receiver on the subject site and back calculation to an acceptable level of risk, to determine the maximum allowable concentration of asbestos fibres in soil.

Relationship between Asbestos Fibre Concentration in Soil and Dust (Field Studies)

A relationship was required to be established between asbestos fibre concentration in soil and asbestos fibre concentration in dust generated from soils. A small amount of work has been undertaken on this previously, and was summarised in Imray and Neville (1993). It had been reported that this relationship was highly variable and dependent upon several factors.

A relationship between asbestos fibre concentration in soil and dust was developed for this risk assessment by undertaking site specific field trials. These field trials incorporated the simulation of construction works on an area of the site known to be impacted with asbestos fibres. Equipment and activities simulated during the field trial were based on the observation of construction works on similar style redevelopment sites. Several activities typically incorporated within such works were simulated (e.g. loading of tippers, track compaction of surfaces, smoothing of soils, tracked equipment movement across soils).

In total, four trials were undertaken. The concentration of asbestos fibres in the soil within the trial area was determined at the completion of the second trial and the fourth trial. Five soil sampling locations on a grid basis were taken at each time. During the trial, air sampling was undertaken at six downwind locations and one upwind location (taken as a control to measure dust or fibres moving onto the trial area). The downwind locations were arranged in a formation somewhat similar to a 'slips cordon'. Each of these sampling locations was provided with an inspirable dust sampler and a fibre sampling cassette. For each sampling location the weight of dust collected and the number of fibres collected during each trial was determined. From comparison of these values the proportion of asbestos fibres in the dust collected was determined. Further comparison of this to the proportion of asbestos fibres in the soil used for the trial allowed the determination of a site-specific relationship between asbestos fibre concentrations in soil and asbestos fibre concentrations in dust generated.

As discussed, four trials were undertaken, and the most conservative results as calculated from the trials were used for the remainder of the assessment. The result as calculated was similar to the range of results as reported in the Imray and Neville (1993) paper.

Estimation of Site Dust Generation

The amount of asbestos fibres that a person would be exposed to from a site would be directly proportional to the amount of dust that same person is exposed to from a site. Hence the dust generation of the site was required to be estimated for a typical lifetime exposure.

It was proposed that the site was to be developed in a staged manner, with persons potentially moving onto the site prior to the development of other areas of the site. As such, persons could be exposed to dust generated during construction works on adjoining areas of the site, and dust generated by fugitive or other sources during the post development phase of the site.

The dust generated during construction works on the site was estimated from the dust generation data obtained during the field trials on the site (where construction activities were simulated). This dust emission rate was found to be similar to those provided in the USEPA (2000) document AP42, for dust emissions from construction sites with no dust controls. It was assumed that construction works occurred 12 hours a day, seven days a week, as per the timescale and staging plan provided by the development manager. It was further assumed that no dust controls were in place during the construction works.

The dust generated during the post development phase of the site (i.e. subsequent to the completion of all construction works and houses) was assumed to be primarily attributable to fugitive dust impacts. Fugitive dust generation rates for the developed site were estimated using the method provided in AP42 with site-specific data (i.e. moisture content, silt content etc.). It was assumed here that no or very little vegetation existed on the site, and the entire site ground surface was disturbed an average of once a week.

It was also assumed that fugitive dust generation would occur during the construction works. With this it was further assumed that the ground cover on the site was disturbed an average of two times during each day and once during each night during the construction works. It was assumed throughout the dust generation calculations that no rainfall occurred.

Calculation of Asbestos Fibre Exposure

The asbestos fibre exposure was required to be calculated for the most affected potential resident on the site as a function of the asbestos fibre concentration in soil. A relationship between asbestos fibre concentration in soil and asbestos fibre concentration in dust generated had been determined from the field trials, as described. The dust generation of the site had been calculated for all phases of a lifetime exposure from the site. Dust dispersion was required to be modelled for the most conservative potential resident location on the site. From this, dust and asbestos fibre exposure would be able to be calculated for a typical lifetime period, as a function of asbestos fibre concentration in soil.

A modelling package was developed for the site configuration incorporating the data obtained during the field trials and previous site contamination assessments, using Visual Basic. This modelling package allowed for placement of potential residents anywhere on the site and accounted for differing exposure to site construction and post development periods that occurred at each location on the site. This was required to account for whether a resident would be exposed to the bulk of the construction works caused by the remainder of the staged development, or if a resident moves onto the site near the completion of the staged development works and is only exposed to a short duration of construction works.

The modelling package utilised dispersion algorithms as provided with the GRI Box Model (1998). The box model was utilised as it has been purpose designed to model dispersion over short distances, and is known to be conservative. As the modelled receivers were generally located on the site, dispersion of dust and asbestos fibres would be expected to occur over short distances. The box model provides dispersion estimates for distances between 10 and 100 m. Dispersion over distances greater than this was estimated by assuming dispersion as per a Pasquill-Gifford F Stability Class (overcast night time conditions with minimal wind velocity and dispersion). The modelling package utilised 12 months of six hourly site-specific meteorology records.

Several different receiver locations were modelled using the package to determine the lowest acceptable soil concentration. Acceptable soil concentrations were found to range between 0.052% to 0.100% (based on mass fraction) for modelled residents on the site. Acceptable concentrations were found to range between 0.122% to 0.182% for residents adjoining the site.

An allowable mass concentration of **0.050%** of asbestos fibres was determined as presenting an acceptable level of risk, for future residents, from the soils on the site. This soil concentration will be applied as the remediation criteria for asbestos fibres in soil over the entire site.

IMPLICATIONS

The site-specific risk-based asbestos criterion determined in this study is higher than those discussed by Imray and Neville (1993). As a consequence, the determination of a site-specific remediation criterion has resulted in:

(a) a significant reduction in remediation costs, whilst ensuring protection of future site users;
(b) significant reduction of the impacts of remediation on the surrounding community by minimising exporting and importing of soils; and
(c) complying with the principles of waste minimisation, by not unnecessarily using valuable landfill space.

relatively non-leachable (based on the toxicity characteristic leaching procedure, TCLP) residual quantity of the original contaminant bound to the larger soil particles.

The qualitative modelling framework, Risk Investigation of Site Contamination (RISC) has been used (Shanableh 1997) to assess the relative advantages/disadvantages of the two alternative methods of site remediation. Adoption of RISC for this purpose involves compilation of relevant information related to the post- and pre-treatment risks associated with the contaminated site available from various organisations, databases and literatures. A subjective but systematic approach is then used to assess the overall level of risk to the environment from the contaminated site.

THE CONTAMINATED SITE

The hypothetical site is contaminated with chromium that is known as being carcinogenic. Chronic inhalation of fine-particle chromium compounds in hexavalent form (Cr^{6+}) may result in lung cancer. Even short-term, high level exposure to Cr^{6+} can result in skin ulcers and damage to the kidney, liver and gastrointestinal tract. The presence of Cr^{6+} in water or in the food chain is considered to be highly hazardous. Cr^{6+} is soluble and mobile under aerobic (oxidizing) condition. The level of toxicity and nature of mobility of Cr^{6+} need to be considered in connection with the two alternative treatment measures.

The contaminated site has scattered grass cover and there is a creek used for recreation (e.g. swimming and fishing) 200 m downstream of the site. The land slope towards the surface water is 7% and the minimum depth to the water table is 20 m. The site has no fencing to prevent public access.

RISK ASSESSMENT

The RISC framework considers four areas of risk potential: (a) contamination potential (air, water, soil, and biota); (b) contaminants transport potential; (c) contaminants toxicity potential (quantity, toxicity, and persistence); and (d) human exposure potential. Each of the above areas can be defined by a number of factors as listed in Table 1. For example, surface water contamination potential depends on distance of the contaminated site from the surface water source, surface water use, potential of surface runoff generation, pollution of surface water via air, pollution of surface water by groundwater flow. Each factor listed in Table 1 is also defined by a number of site-specific or generic sub-factors related to the fate, transport, toxicity, and environmental setting. Examples of such sub-factors include: rainfall quantity; land slope towards the surface water; runoff diversion; land cover; direction of groundwater flow; causes of groundwater flow; physical status of the waste; and waste containment.

Risk assessment using RISC requires independent ranking of each factor identified in Table 1. This ranking can be qualitative (i.e. low, medium, high) or based on a scoring system. The ranking of the various risk factors (Table 1) is subjective and the ranks have no absolute meaning. Accordingly, in ranking the various factors, the assessor must qualify the ranking of the different factors (i.e. what constitutes a high, medium, or low ranking). Accordingly, it is important to state the assumptions and specify the uncertainties associated with the assessment.

The RISC framework is in effect a hazard ranking system (USEPA 1986). When the risk levels are identified in Table 1, the likelihood of an exposure through a specified route and via a specified medium is ranked as in Table 2. The overall risk is then qualitatively evaluated according to the superposition principle. This subjective, but systematic procedure, produces an overall ranking of the risk associated with the contaminated site before and after each of the remedial measures.

Risk-Based Assessment of Site Remediation Alternatives

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ABSTRACT: Risk assessment offers a systematic framework for decision making with regards to issues of human health and ecological concern. The risk assessment process can be used to integrate a variety of complex factors relating to public health, ecosystems, technology and public perception. The use of risk assessment as a tool to evaluate site remediation alternatives is also in line with recent developments in Australia which require the use of risk assessment as a framework for assessing contaminated sites and remediation alternatives. In this study, a specific contaminated site risk assessment model was used to assess two contaminated site remedial alternatives. The remediation alternatives are stabilisation and washing of heavy metals in contaminated soils. Using treatability and site specific data, the results demonstrate the effectiveness of risk assessment as a tool for analysis and ranking alternative remedial techniques based on health, ecological and perception criteria.

KEYWORDS: remediation, risk assessment, contaminated sites, soil stabilisation, soil washing

INTRODUCTION

Risk-based approaches offer a systematic framework for decision making with regard to contaminated site remediation. The Australian and New Zealand Environment and Conservation Council (ANZECC) and the National Health and Medical Research Council (NHMRC) originally used a 'criteria-based' approach rather than a 'risk-based' approach for the management of contaminated sites (ANZECC and NHMRC 1992). More recently, Australian federal agencies and states advocate the adoption of risk assessment as a tool for managing contaminated sites (e.g. ANZECC 1996, NHMRC 1997, NSW EPA 1997, QdoE 1998). The basic framework for risk assessment is outlined for Superfund sites by the USEPA (1989).

For the remediation of a particular contaminated site, a number of techniques may be applicable, each with a certain degree of effectiveness to reduce particular risks. The decision to select an appropriate remediation alternative to suit a particular contaminated site is not an easy task and requires assessment of the technical and economic feasibility of a number of alternatives. This paper presents a risk-based approach to select the preferred method of remediation for a chromium-contaminated site. Two alternative remedial measures are evaluated and compared: soil stabilisation and soil washing. Stabilisation attempts to confine the contaminants within the site itself, thus reduces the mobility (i.e., leachability) of the contaminants. However, strong erosion potential (e.g., heavy rainfall, destruction of top cover, movement of heavy vehicles on the contaminated site, on-site construction activity) may result in transportation of finer particles from the site. Washing reduces the quantity of soil contaminants, transfers the contaminants into the washing solution, and generates a residual consisting of contaminated fine soil particles. The result of washing is clean soil containing a

CONCLUSION

No generic criteria exist for maximum allowable concentrations of asbestos fibres in soils on residential sites. Little guidance is provided by regulatory authorities as to what would be a safe level of asbestos fibres.

A risk-based method for determining site-specific maximum allowable concentrations of asbestos fibres in soils has been developed. This method utilises conservative assumptions combined with several pieces of site-specific data. This same approach would be able to be replicated in the assessment of other asbestos fibre impacted sites. The success of this approach is dependent upon the utilisation of the greatest amount of site-specific data possible, and the use of conservative assumptions where site-specific data is not available.

Finally, there can be significant benefits to site owners and the broader community by developing site-specific risk-based criteria for asbestos in soils.

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From Tables 1 and 2, it appears that a notable difference between two remedial measures relates to the 'quantity factor'. In soil stabilisation, the quantity of contaminant remains the same. Although stabilisation restricts the transportation of the contaminants, heavy rainfall may cause erosion of finer particles from the site and high water table conditions may result in transportation of contaminants to the nearby surface water. Also, children are at higher risk, as access is not restricted to the site. In the case of soil washing, the major risk relates to the disposal of extracted contaminants and it is assumed that the contaminants will be disposed of in a hazardous waste landfill.

Table 1. Qualitative risk characterisation for two site remediation alternatives

Factor	Rank			Remark
	Before treatment	Soil stabilisation	Soil washing	
Assess the Air Contamination Potential				
1. Chemical volatilisation	Low	Low	Low	Non volatile.
2. Dust/particles release	High	Low*	Low	Scattered grass covers. Heavy wind, erosion, vehicular movement may release finer particles. * Stabilised soil covered.
3. Contaminant exposure to atmosphere	High	Low	Low	Stabilised soil covered.
Assess the Surface Water Contamination Potential				
4. Distance from the contaminated site	Medium	Medium	Medium	Surface water within 200 m.
5. Exposure/ease of transport of contaminants	High	Low	Low	Loose finer particles may reach to surface water.
6. Surface water use	Medium	Medium	Medium	Surface water used for recreation.
7. The potential for runoff, overland flow and erosion	High	Low-Med	Low	7% land slope towards surface water, heavy rainfall event may cause erosion of finer particles from stabilised site.
8. Pollution via air	Medium	Low	Low	Low air pollution potential.
9. Pollution via underground water flow	Medium	Low-Med	Low	Flow may occur during high water table condition.
Assess Groundwater Contamination Potential				
10. Distance/ease of transport of chemicals from the contaminated site	Medium	Low	Low	Water table more than 20 m deep.
11. Permeability/ease of transport of contaminants in the unsaturated zone	Medium	Low	Medium	$1x10^{-5}$ < permeability < $1x10^{-3}$.
12. Ground water use	Low	Low	Low	Not used.
13. Leachate generation	Medium	Low	Low	Contaminated material stabilised.
Assess Soil Contamination Potential				
14. Surface soil contamination	High	Low	Low	Contamination detected.
15. Detected surface soil contamination	High	Med	Low	Soil contamination detected.
16. Subsoil contamination	Medium	Low	Low	Average permeability, low leachate generation potential, average rainfall, no contamination detected below 30 cm

Assess Biota (Food sources) Contamination Potential				
17. Biota contamination via direct contact	Low	Low	Low	Distant food sources.
18. Biota contamination via contaminated surface water	Low-Med	Low	Low	Surface water contamination potential exists, recreational fishing.
19. Biota contamination via air	Low-Med	Low	Low	Low air contamination potential, distant food sources.
Assess Contaminant Transport Potential				
20. Transport via air	Medium	Low	Low	Low contamination potential.
21. Transport via groundwater	Low-Med	Low	Low	Low contamination potential.
22. Transport via surface water	Med	Low	Low	Medium contamination potential.
23. Transport of contaminated material by human activity	Low-Med	Low	Med-High*	No active soil transport off site. *Contaminated soil particles disposed off in a hazardous waste landfill.
24. Transport by movement of exposed organisms	Low- Med	Low	Low	Domesticated animals potentially exposed but transport potential is low.
Assess Population Exposure Potential				
29. On-site population factor	Medium	Low-Med*	Low	* Access not restricted.
30. On-site population activity factor	High	Low-Med*	Low	*Access not restricted.
31. Nearby population	---	---	---	
32. Nearby population activity	---	---	—	
33. Distant population	---	---	—	
34. Subpopulation	High	Low-Med*	Low	*Children may inhale loose particles, come in contact with soil.
35. Subpopulation Activity	High	Low-Med*	Low	Children play grounds. Access not restricted.
36. Future population	---	---	---	
37. Future population activity	---	---	---	
Assess Chemical Toxicity Potential				
38. Potential exposure levels in the various media (quantity factor)	High	Medium	Low	Total contamination estimated to be 30 kg.
39. Inherent chemical toxicity hazard (for non carcinogens)	---	---	—	Carcinogenic material.
40. Inherent chemical toxicity and weight of evidence (for carcinogens	High	High	High	Carcinogen.
41. Persistence of the chemical in the various media	High	High	High	

A risk scoring method may be applied to make a comparison between the remedial measures. For example, risk scores of 20, 10, 5 and 0 may be assigned tentatively for high, medium, low-medium and low levels of risks, respectively. The aggregated risk levels, without using a weighting factor, are compared in Fig. 1 for three cases: before treatment, soil stabilisation and soil washing. From the results of a survey conducted among 20 randomly selected people, it appears that washing is the preferred option of remediation on the basis of perception.

Table 2. Relative risk characterisation summary for two site remediation alternatives

Exposure route	Rank			Remark
	Before treatment	Soil stabilisation	Soil washing	
Drinking water	---	---	---	Water not used for drinking.
Ingestion while swimming/water	High	Low	Low	Children more vulnerable.
Dermal contact/water	High	Low	Medium	Children more vulnerable.
Ingestion/soil	High	Low-Med	Low	Access not restricted, children play activity.
Dermal contact/soil	High	Low-Med	Low	Access not restricted, children play activity.
Inhalation/air	High	Low-Med	Low	Finer particles may release from the stabilised site.
Ingestion/fish and shell fish	High	Low-Med	Low	Surface water has medium contamination potential, fishing activity, children more vulnerable.
Ingestion/fruits & vegetables	Low	Low	Low	Fruits and vegetables from distant source.
Ingestion/meat, eggs, and dairy products	Low	Low	Low	Products from distant source.

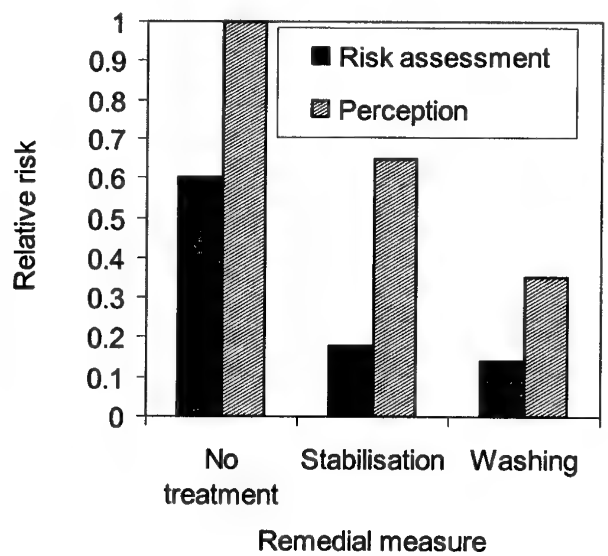

Fig.1. Relative risk levels associated with the remedial measures

DISCUSSION

The RISC framework can be used to develop a database for a contaminated site from all available sources of information. A fair degree of subjectivity is involved with the process, and the assessor needs to use their best judgement to complete the assessment. The assembled

data can be evaluated to gain a conceptual understanding of the risk posed by the contaminated site before and after alternative remedial measures. The outcome of this preliminary assessment helps to identify further data requirements and appropriate detailed investigation.

CONCLUSION

The paper demonstrates how a risk-based modelling framework can be used to compile the relevant information relating to the risks from a contaminated site and also how two alternative site remedial measures can be compared to select the more appropriate one. The method helps to integrate a variety of complex factors relating to public health, ecosystems and environment relevant to contaminated site remediation. The results of the case study presented here is based on subjective judgement and is not strictly applicable to any particular contaminated site though the general methodology can be used to a specific problem.

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A Joint Probability Approach to Assess Risk to the Environment from Contaminated Sites in a City Area

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ABSTRACT: Application of risk-based approaches to environmental risk assessment from contaminated sites is a growing area of research. A joint probability approach offers a theoretically superior method of risk assessment that considers the probability distributed nature of the risk factors to obtain probability distributed risk output. The method is particularly useful when the data related to the contaminated sites are scarce and a risk factor is better described by a probability distribution rather than a representative single value. This paper describes a modelling framework based on the joint probability approach that can be applied in a systematic manner to assess the overall risk to the environment from a group of contaminated sites in a city area.

KEYWORDS: contaminated sites, joint probability approach, risk assessment, landfill, probability distribution

INTRODUCTION

Most city authorities manage contaminated sites that were not designed and constructed in an engineered manner. For example, Brisbane City Council manages 150 closed landfills with no base liners or extensive leachate collection systems (Brisbane City Council 2000). This type of contaminated site is a potential risk to the environment and public health in the city area. A risk-based approach is a powerful tool to assess risk to public health and the environment from contaminated sites. The Australian and New Zealand Environment and Conservation Council (ANZECC) and the National Health and Medical Research Council (NHMRC) originally used a 'criteria-based' approach rather than a 'risk-based' approach for the management of contaminated sites (ANZECC and NHMRC 1992). More recently, Australian federal agencies and states advocate the adoption of risk assessment as a tool for managing contaminated sites (e.g. ANZECC 1996, NHMRC 1997, NSW EPA 1997, QDoE, 1998).

This paper presents a risk-based modelling framework based on the joint probability approach where a risk characteristic (e.g. age of a landfill, percent industrial waste in a landfill) is described by a probability distribution rather than a point estimate. The output of the risk calculation is also expressed in the form of a probability distribution. The application of probability distributions enables the uncertainties associated with the input risk characteristics to be taken into account to obtain more realistic output. There are examples where the joint probability approach has been applied in risk assessment. For example, Leonte and Tehrani (1996) adopted a Monte Carlo simulation technique to develop health-based cleanup levels for the chemicals of concern. Wright and Howell (1996) illustrated how a Monte Carlo simulation technique can be used in the health risk assessment.

The present paper, in particular, outlines how the Joint probability approach can be used to assess the overall risk to the environment from a group of contaminated sites in a city area. The adopted method uses a subjective but rational and consistent risk scoring system to

integrate risks from the possible risk characteristics over all the contaminated sites in a city area to estimate overall risk to the environment.

THE MODELLING FRAMEWORK

Let there be N contaminated sites in a city area. For each site, there are L risk characteristics and for each of the risk characteristics, there are k levels of risk X (e.g. very high: score 20, high: score 15, medium: score 10, low: score 5). The gross risk score (GRS) for a contaminated site j may be estimated by:

$$GRS_j = \sum_{i=1}^{L} X_i \tag{1}$$

The data for a risk characteristic may not be available for all the N sites, only a reasonable upper and lower limit and a mean value may be assumed. Using the available data, the risk characteristic may be described by a probability distribution. A Monte Carlo simulation technique may be applied to generate data from the distribution of the risk characteristic. Each run of the Monte Carlo simulation from the distributions of all the risk characteristics would represent a typical contaminated site. A large number of runs (M) may be considered to capture the full variability and uncertainty associated with the distributions of the risk characteristics. For each of the M simulation runs, gross risk score (GRS) may be computed using Eqn (1).

The M values of GRS or selected statistics may be subjected to a frequency analysis. The resulting histogram and/or the frequency curve may be used to estimate the overall risk to the environment from the N contaminated sites.

AN EXAMPLE

Consider a city area has 100 landfills, which have no base liners and leachate collection systems. The risk characteristics of the landfills may be: (a) age of the landfill; (b) distance of the landfill from the nearest suburb; (c) thickness of the final cover; (d) fraction of industrial waste in the landfill; (e) average depth to groundwater table; (f) average annual rainfall on the landfill; (g) distance of the landfill from the surface water source e.g. creek, stream; and (h) average thickness of the vegetation cover.

The data for the eight risk characteristics are collected for all the 100 landfills. If the data are not available for a particular risk characteristic at a landfill site, professional judgement may be used to assume a reasonable value. The distribution of a risk characteristic can be determined from the respective histogram obtained from the collected data. For each of the eight risk characteristics, level of risks may be selected as illustrated in Table 1. The probability distributions of the risk characteristics may be obtained as illustrated in Fig. 1.

From the identified probability distributions, data may be generated (according to the probability of occurrence of a risk characteristic) to represent a typical contaminated site e.g. the jth generation represents a contaminated site with risk characteristics as shown in Table 2.

Table 1. Risk levels associated with the risk characteristics

Risk characteristics and range of values	Risk level	Score	Risk characteristics and range of values	Risk level	Score
Age (years) of the landfill:			Average depth (m) to groundwater table:		
<5	Very high	20	<1	Very high	20
5-10	High	15	1-2	High	15
11-15	Medium	10	2-3	Medium	10
>15	Low	5	>3	Low	5
Distance (km) of the landfill from the nearest suburb:			Average annual rainfall (mm) on the landfill:		
<2	Very high	20	>2000	Very high	20
2-5	High	15	1500-2000	High	15
6-10	Medium	10	1000-1500	Medium	10
>10	Low	5	<1000	Low	5
Thickness (mm) of the final cover:			Distance of the landfill (m) from surface water source:		
<25	Very high	20	<50	Very high	20
25-50	High	15	50-100	High	15
51-75	Medium	10	100-500	Medium	10
>75	Low	5	>500	Low	5
Fraction industrial waste in the landfill:			Average thickness (mm) of the vegetation cover:		
>0.50	Very high	20	<100	Very high	20
0.30-0.50	High	15	100-300	High	15
0.10-0.29	Medium	10	300-500	Medium	10
<0.10	Low	5	>500	Low	5

The GRS value for the *j*th landfill is 110, 'contamination severity' may be computed as GRS divided by total possible score i.e. 110/160 = 0.69. The *M* values (*M* in the order of thousands) of contamination severity may be used to generate a frequency curve as illustrated in Fig. 2. This frequency curve indicates the overall risk level to the environment from the group of contaminated sites. For example, an exponential shape of the frequency distribution would indicate a 'low' overall risk and a thick tail would indicate a 'high' overall risk to the environment.

Table 2. Generated data for a typical landfill

Risk characteristics	Generated data	Risk level	Score
Age of the landfill	12 years	Medium	10
Distance of the landfill from the nearest suburb	1 km	Very high	20
Thickness of the final cover	78 mm	Low	5
Fraction industrial waste	0.41	High	15
Average depth to groundwater table	1.75 m	High	15
Average annual rainfall	900 mm	Low	5
Distance from the surface water	26 m	Very high	20
Vegetation cover	77 mm	Very high	20

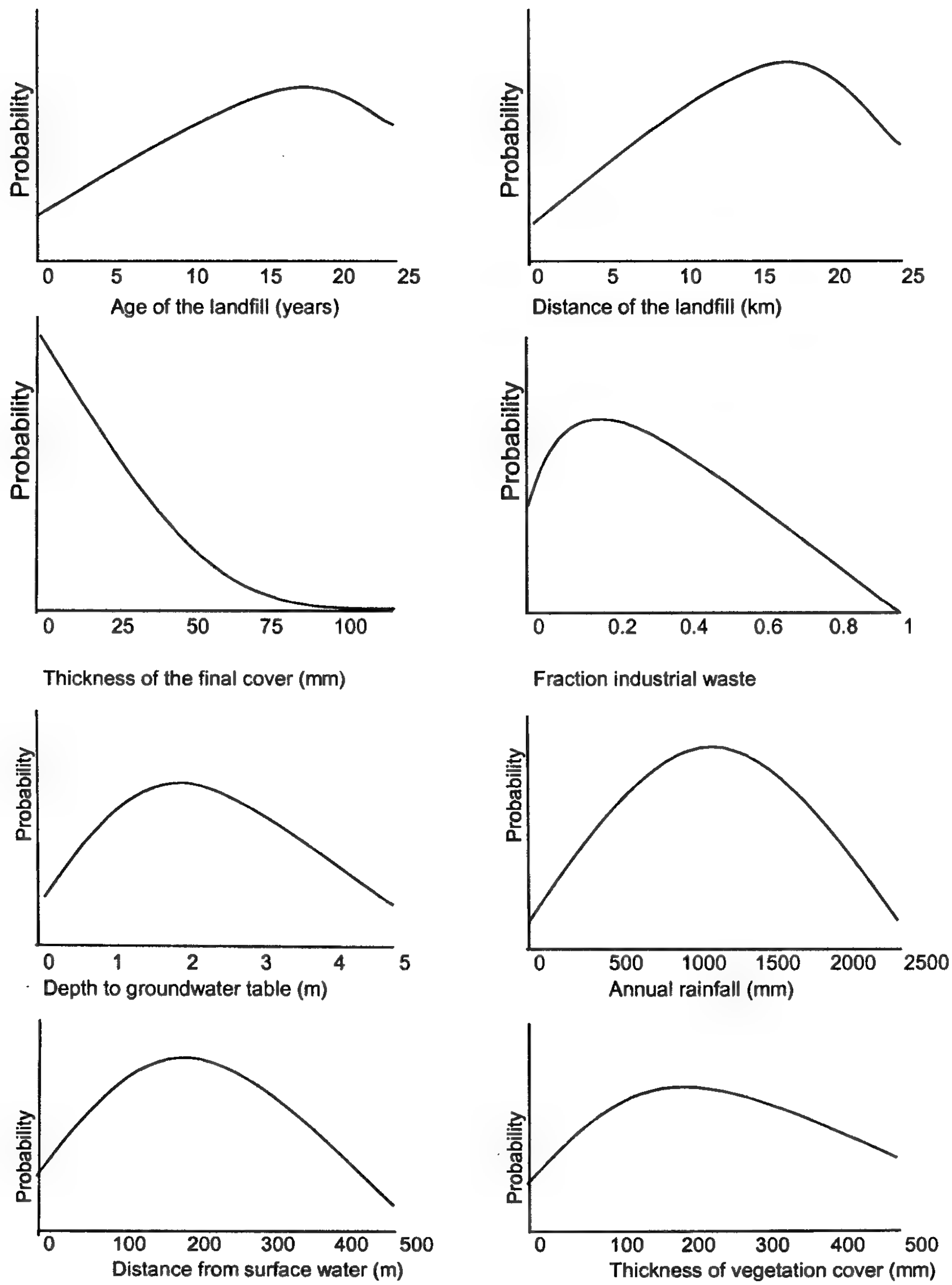

Fig. 1. Probability distributions of the risk characteristics

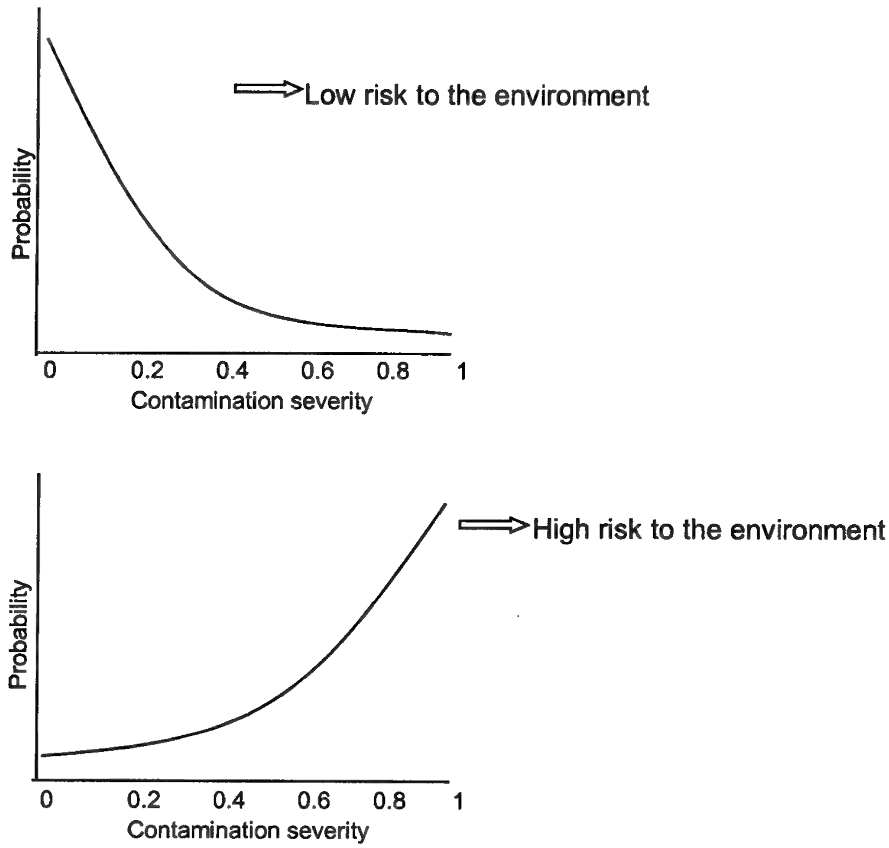

Fig. 2. Frequency curve indicating overall risk to the environment from the contaminated sites

The ranking of the various risk characteristics as adopted here is subjective and ranks do not have any absolute meaning. Accordingly, the assessor must understand the ranking of the various factors (i.e. what constitutes a very high, high, medium or low ranking). Also the scoring system is tentative and a different scoring may be appropriate for another application. A weighting factor may need to be considered for real applications.

CONCLUSION

The paper outlines the application of joint probability approach in the assessment of overall risk to the environment from a group of contaminated sites. The particular strength of the technique is that it can account for the probability-distributed nature of a risk characteristic and provide more realistic risk outcome. The method, however, is computationally intensive and needs subjective professional judgement to compensate for the lack of data and identify the most appropriate probability distribution for a particular risk characteristic. The interactions between various risk characteristics may need to be considered for some applications by using the concept of conditional distributions. The assumptions and

limitations of the approach should be taken into account to interpret the final outcome of Monte Carlo simulations.

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How Hazardous are Arsenic Contaminated Mine Spoils in Victoria?

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ABSTRACT: Soil from historical gold mining sites in Victoria has been analysed for total and water-soluble arsenic concentrations. Samples were selected from a range of sites throughout Victoria containing alluvial, mullock, quartz tailings and residues from roastings of sulfide rich gold ore. Total arsenic concentrations ranged from 2.6 ppm in alluvial materials up to 16600 ppm on smelter residues, with the majority of quartz tailings sites recording levels in the range 200 - 2500 ppm. The results from the preliminary stage of the project will be used to select sites for further sampling and analysis, prior to commencing a pot experiment that aims to assess the uptake of arsenic by vegetables.

KEYWORDS: arsenic, contamination, mine wastes, soil, Victoria

INTRODUCTION

The importance of arsenic as a hazardous metal in soil and water has been brought to prominence by the chronic nature of the problem in India (Chowdhury *et al.* 1997) and Bangladesh, where groundwater As levels are commonly in excess of WHO permissible limits. While arsenic concentration in drinking water can be directly related to human health, arsenic concentration in soil is less well understood as a health hazard. Cobb *et al.* (2000) studying uptake of heavy metals in vegetables grown on mine wastes, have shown that sensitivities to As as a phytotoxin, and tendencies to concentrate and translocate As in tissue are species dependent. The ANZECC/NHMRC health limit for As in soil is currently 100 mg total As kg^{-1} (ANZECC/NHMRC 1992), and this level is known to be frequently exceeded in a number of Australian environments (Hinwood *et al.* 1998). Research is needed to establish the risk that this presents to human health in Australia.

Arsenic in Gold Mine Wastes in Victoria

The work reported here presents data for a number of As-contaminated soils taken from gold mine wastes in Victoria.

Gold mine wastes in Victoria in this study are characterised as:

(a) old alluvial gold mine materials, such as pebbles/cobbles and fine residues (slums) derived from sluiced alluvium which was sourced from modern stream alluvium or ancient buried river deposits (i.e. palaeoplacers, including 'deep leads');
(b) battery (i.e. mill) sands (tailings) derived by crushing of gold bearing quartz veins (reefs);
(c) waste rock (mullock) produced during quartz reef mining; and
(d) residues from roasting of sulphide-rich gold ore (smelter residues).

High concentrations of arsenic are frequently associated with gold bearing ore, most commonly as arsenopyrite (FeAsS). Hughes *et al.* (1997) have demonstrated that the most widespread mineralogical style of gold mineralisation in the Victorian gold province is the simple pyrite-arsenopyrite type. Consequently Victorian gold mines produce waste materials such as waste rock and tailings with high arsenic concentrations.

Historical mining operations typically disposed of waste tailings without regard to the environment, with tailings and smelter residues being pumped down creeks, or left in unvegetated mounds of blowing sands. Many housing developments have been constructed over or near such residues associated with abandoned mine tailings, with potential risks to health associated with exposure to elevated levels of arsenic (Hinwood *et al.* 1998).

This project, funded by ACIAR, will evaluate As hazard in these mine wastes through measurement of uptake by vegetables grown in mine tailings.

METHODS

Twenty sites were selected from known areas of historical gold mining activity, identified by a review of literature on historical gold mining activities in Victoria (e.g. Stone and Dunnett 1993), and regional geological maps (e.g. Willman and Wilkinson 1992). Sites included Stawell, Ballarat, Maldon, Bendigo and Bethanga.

Surface soils were collected from each site, with some sites sampled to depths of 0.5 m. At two sites, additional samples were taken from land adjacent to the mine spoils to assess the degree of off-site contamination with arsenic by wind or water deposition.

Total arsenic was determined by digesting soil with concentrated nitric and hydrochloric acids and analysed by atomic absorption spectrometry (AAS) with a detection limit (DL) of 0.7 ppm.

Water-soluble arsenic was determined on a 1:5 soil:water suspension by hydride generation AAS (DL= 0.13 $\mu g\ L^{-1}$).

RESULTS

Table 1 shows the range of total and water-soluble arsenic concentrations of the different types of mine material sampled, and Table 2 shows As values for soil material adjacent to two areas of mine spoils.

Table 1. Arsenic concentrations of historical gold mine material (ppm)

	Total As Range (Median)	Water-Soluble As Range (Median)	No. of sites
Alluvial mine material	2.6 – 7.7 (4.8)	DL – 0.002 (DL)	4
Mullock from quartz mines	48.9 – 61.7 (50.6)	0.002 – 0.273 (0.009)	3
Battery sands and quartz tailings	280 – 2491 (905)	0.015 - 4.14 (0.70)	14
Residues from roasting	6252 – 16000 (11126)	1.9 – 11.1 (6.5)	2

Table 2. Arsenic concentrations of soil material adjacent to two mine spoil sites (ppm)

Source of sample	Total As	Water-soluble As
50 m downslope of 16000 ppm 'roastings'	809	0.797
100 m downslope of 16000 ppm 'roastings'	239	0.334
Creek alluvium reported as sludge - contaminated (1850s) from maps of Peterson (1996)	434 - 1228	1.10 - 2.43
Creek alluvium reported as non-contaminated from maps of Peterson (1996)	10.2 - 48.0	0.016 - 0.121

DISCUSSION

Alluvial Mine Material

Concentrations of As in the alluvial gold mine material were found to be below ANZECC/NHMRC guidelines for soil of 100 mg total As kg^{-1} (ANZECC/NHMRC1992). This reflects the geological history of the material. During the exposure, fragmentation, hydrolysis, oxidation and transportation of the gold bearing rock, arsenic would become soluble and be leached away. Therefore it is not expected that As concentrations would be high in alluvial material.

Waste Mine Rock

The three waste rock sites contained material derived from quartz reef mining, so it is expected that As levels in such dumps would be higher than in waste rock from deep leads and alluvial deposits. The total As levels in this material was found to be below that considered a health hazard (ANZECC/NHMRC 1992), however, this could vary with provenance of the rock and higher levels may exist in waste rock dumps.

Battery Tailings Sands and Residues from Roastings

All of the sites containing tailings sand and smelter residues exceeded the ANZECC/NHMRC guidelines for soil of 100 mg total As kg^{-1} (ANZECC/NHMRC 1992). Arsenic is found in natural geological association with gold mineralisation and therefore the As concentration of mine tailings and waste material are principally governed by the original concentration in the ore material. The data show a wide range of concentrations, reflecting the different geological matrices from which the material has been derived.

The high As concentrations of the battery sands and tailings and the residues from roastings appear to be phytotoxic to most plant species. Many of the sites are totally bare or scarcely vegetated, making them vulnerable to erosion by wind and water. During summer, dust containing high levels of As may blow over nearby residential areas. This poses a potential health risk to surrounding residents.

The extreme concentrations of As found in the residues of the roasted material (16600 ppm) is reflected in the highest water soluble As level (11.1 ppm). The proportion of water soluble As to total As at this site is lower than the majority of the other sites, suggesting that the As is more tightly bound within this material. It is expected that the Fe-oxide content of

this material is high due to the geological nature of the original ore material, therefore adsorption of arsenic onto insoluble hydrous Fe-oxide species is probable.

Adjacent Soil Materials

The two samples taken 50 and 100 m downslope of the roasting material (16000 ppm) have elevated levels of total As, 809 and 239 ppm respectively. These results have implications for the surrounding residential properties, which are as close as 30 m to the smelter residues.

The creek alluvium contaminated with sludge also exceeds the ANZECC/NHMRC guidelines. During the 1850s, sludge residual from the puddling phase of the gold mining in the Bendigo area was deposited directly into the Bendigo Creek. Original maps of this sludge have recently been updated by Peterson (1996) and is reported to cover 700 km^2. Although alluvial slums of this type probably contain little As, quartz tailings mixed with this material are the probable source of the elevated As values observed. This has implications for both residential and farming properties located along the creek.

CONCLUSIONS

Historical mining operations on gold-bearing quartz reefs have lead to high concentrations of arsenic at old mining sites throughout Victoria. The highest concentrations are present in roasted sulphide residues, although concentrations in all quartz mine tailing samples exceed recommended health levels for soil. Arsenic has also dispersed into soils adjacent to the mine materials. Further sampling and characterisation of the mine materials with regard to the available arsenic concentration and associated mineral complexes is needed to fully understand the potential health and environmental implications.

The majority of the sites sampled for this report are close to residential properties, therefore it is likely that many gardens also have high arsenic concentrations with implications to human health through the possible uptake of arsenic by vegetables. This is the rationale for proposed pot trials of vegetables grown in mine tailings from the Victorian goldfields.

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Contaminant Water Chemistry and Distribution of Fishes in the East Branch, Finniss River, Following Remediation of the Rum Jungle Uranium/Copper Mine Site

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ABSTRACT: Unabated acid rock drainage contaminants from the Rum Jungle mine site led to the virtual absence of fishes from the exposed region of the East Branch, Finniss River, during 1973 and 1974. Following the initiation of mine site remediation in 1982 the measured annual contaminant loads delivered to the East Branch have declined, and there have been marked reductions in their highest water concentrations. Field studies during the 1993 dry season have demonstrated the occurrence of five fish species in the contaminated region of the East Branch, confirming a degree of post-remedial ecological recovery. These species penetrate to varying degrees upstream along a concentration gradient of water contaminants, with one species (*Melanotaenia nigrans*) being still present in abundance at the following dissolved water concentrations: Cu - 1.36 mg L^{-1}; Zn - 1.7 mg L^{-1}; Mn - 4.7 mg L^{-1}. These occurrences indicate that varying degrees of tolerance to the contaminant water concentrations have developed among these fishes.

KEYWORDS: mining, uranium, metals, fish, freshwater, remediation, recovery

INTRODUCTION

The Rum Jungle uranium/copper mine in tropical northern Australia has been a source of acid rock drainage (ARD) contaminants since the 1950s, which have had adverse impacts on the receiving waters of the Finniss River. During the late 1960s/early 1970s unabated contaminant loads from Rum Jungle were quantified, and the geographical scale and intensity of detriment to the aquatic biota of the Finniss River was investigated. Fish diversity and abundance was virtually eliminated in the contaminated region of the East Branch during this period (Davy and Jones 1975, Jeffree and Williams 1975, 1980). Mine site remediation began in 1982 and has been followed by intensive monitoring of water quality and flow. These data have been used to determine both annual-cycle contaminant loads and frequency distributions of contaminant water concentrations, and their changes following remediation (Jeffree *et al.* 2000). Investigations have also been undertaken to measure aspects of the post-remedial ecological status of the Finniss River system (Jackson 1993, Zuk *et al.* 1994, Jeffree *et al.* in press).

In this study we describe (a) the water concentrations of mine-related contaminants in the impacted region of the East Branch during the 1993 dry season, a decade after the initiation of the remedial activities at Rum Jungle, and (b) the distributions of five species of fish in relation to this post-remedial pollution gradient.

METHODS

Sampling Sites

Figure 1 shows each of the sites on the East Branch from which fishes were sampled for this study, including sites 1-6 in the main channel of the East Branch, downstream of RJ and site 8, upstream of RJ. Other sites not exposed to mine-related contaminants were 2s, 4s, 4A and 4As, which occur on smaller side streams.

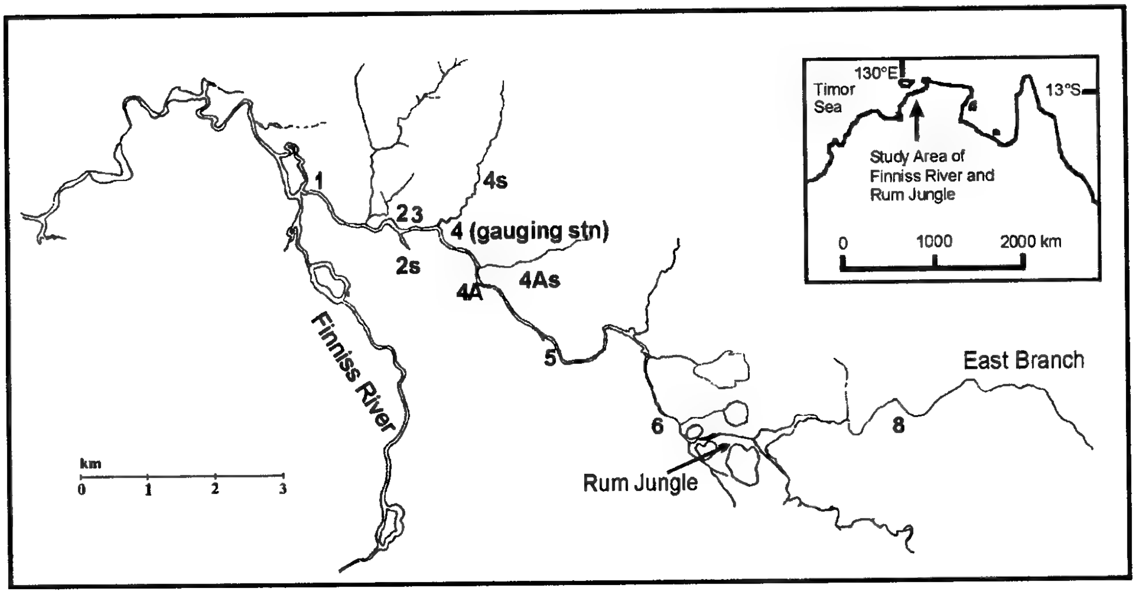

Fig. 1. Map of the Finniss River system showing sampling sites on the East Branch

Physico-chemical Sampling

Water quality measurements and duplicate sub-surface water samples for chemical analyses were taken at each of these sites (Fig. 1). Temperature, conductivity, dissolved oxygen, pH and turbidity were measured *in situ* with a Horiba U-10 water quality meter. Water samples were analysed by ICP-MS and ICP-AES for Cu, Zn and Mn, as well as Ca, Mg and Na.

Sampling of Fishes

Eleven sites were sampled in East Branch including those above (8) and below (1, 2, 3, 4, 4a, 5, 6) the mine-site, as well as side streams (4, 4a, 2) unexposed to contaminants from the mine-site. Sampling was conducted by the seining of measured lengths and breadths of stream sections to obtain semi-quantitative measures of their abundances and distributions, relative to contemporary contaminant concentrations in water (Jeffree and Williams 1980). One species, the spangled grunter (*Leiotherapon unicolor*) was also observed at two sites, although it eluded capture.

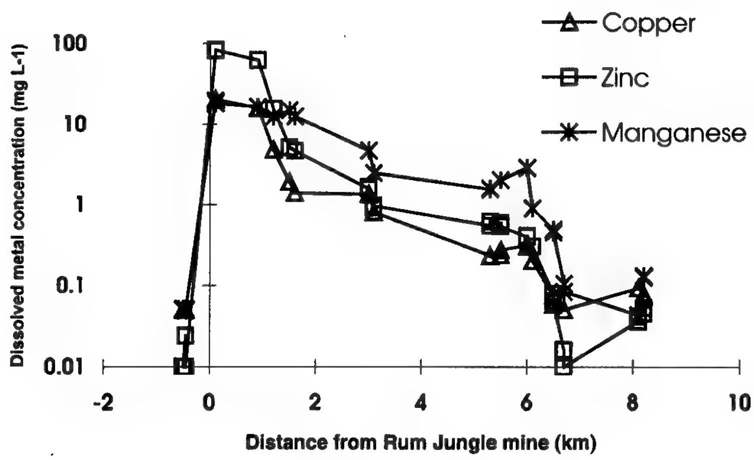

Fig. 2. Metal water concentrations in the East Branch as a function of distance downstream of the Rum Jungle mine site

RESULTS

Physico-chemical Measurements

Figure 2 shows a plot of the dissolved water concentrations of Cu, Zn and Mn measured in the East Branch proper as a function of distance downstream of the Rum Jungle mine site. Their concentrations increased by two or more orders of magnitude immediately downstream of the mine-site, compared to upstream sites, and then declined appreciably with distance downstream. This decline is particularly evident at the site immediately below a perennial spring, 6.6 km downstream from the mine site.

In Fig. 3, the dissolved Ca, Mg and Na water concentrations are shown plotted as a function of distance downstream of the mine site. Their concentrations are enhanced by about an order of magnitude downstream of the mine site, relative to immediately above the mine-site. Their levels decline towards background concentrations with distance downstream of the mine-site. There was also a general trend of increasing pH with increasing distance downstream of the minesite. However, there was no significant ($P>0.05$) difference in pH between sites exposed and unexposed to mine waste contaminants.

Within the East Branch, conductivity values reached a maximum of 3.5 mS cm^{-1} at site 6 (Fig. 1) and decreased with increasing distance downstream of the mine site, to 0.66 mS cm^{-1} whereas control sites ranged between 0.03-0.34 mS.cm^{-1}. Turbidity ranged from 0.00 to 10.0 NTU among all sites, with higher values generally recorded in the side streams. Oxygen saturation was generally higher at sites exposed to contaminants (59-131%) than unexposed sites (27-103%). Water temperatures varied between 22-29.8°C, with sites exposed to contaminants having significantly ($P>0.05$) elevated values, compared to unexposed sites. This may be in part due to increased insolation as a consequence of reduced density of bank-side vegetation, due to pollution loads (Jeffree and Williams 1975, 1980).

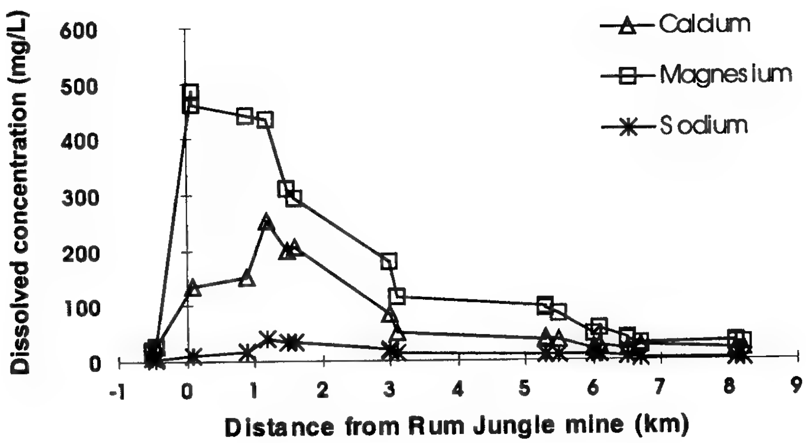

Fig. 3. Ca, Mg and Na water concentrations in the East Branch as a function of distance downstream of the Rum Jungle mine site

Distribution of Fishes

In Table 1, the occurrence of fish species is shown for each of the sampled sites in the East Branch proper, as well as smaller side streams. These data show that five species of fish occurred in the East Branch proper downstream of RJ. The number of species increased with distance downstream of RJ, coincident with the decline in contaminant water concentrations (Figs 2 and 3). However, species did occur at very high contaminant concentrations. *Melanotaenia nigrans* was found in small schools only 2.5 km downstream of RJ between sites 5 and 6 (Fig. 1), where dissolved water concentrations of metals were: Cu - 1.36 mg L^{-1}; Zn - 1.66 mg L^{-1}; Mn - 4.7 mg L^{-1}. Moreover, single individuals of this species were found further upstream swimming normally at three times these water concentrations, but were not observed at higher levels of contaminants.

Table 1. The occurrence of fish species at each sampling site within the East Branch, Finniss River (Fig. 1; site codes for side streams in italics)

Site code	Fish species *Melanotaenia nigrans*	*M. s. splendida*	*Mugurnda mogurnda*	*Leiopotherapon unicolor*	*Ambassis macleayi*
1	↓	↓	↓	↓	↓
2	↓		↓	↓	
3	↓	↓	↓		
4	↓	↓			
4A	↓	↓			
5	↓				
6					
8	↓		↓		
2s	↓	↓	↓		
4As	↓	↓	↓		
4s	↓	↓	↓		

DISCUSSION

Pre-remedial investigations on the distribution of fishes in the EB during comparable periods of 1973 and 1974 showed that they were virtually absent from its contaminated region, where contaminant water concentrations had the following ranges (mg L^{-1}): Cu, 0.03-250; Zn, 0.02-12 and; Mn, 1.5-50. However, the species *M. nigrans, M. mogurnda, Ambassis sp.* and *Synbranchus sp.* were found in its tributaries during the Dry season of 1974. Moreover, dead and/or moribund *M. nigrans,* were observed in the EB in proximity to junctions with its tributaries near sites 4, 3 and 2, where its populations were abundant and vigorous (Jeffree and Williams 1975). Their mortalities in the East Branch proper were consistent with its highly toxic nature. During the period of post-remedial sampling there has been very appreciable reductions in contaminant water concentrations, consistent with the measured reductions in their annual loads being delivered to the East Branch, following remediation (Jeffree *et al.* 2000). However, the highest Cu concentrations at which fish still occur are approximately 8 times higher than the median LC_{50} derived from 133 literature values of lethal toxicity (7-78 day exposures) to bony freshwater fishes. These data were collated for the currently proposed revisions to the Australian and New Zealand water quality guidelines and are available with the ecological risk assessment code, AQUARISK (Twining *et al.* 1999). The code was also used to derive a log-normal distribution function for the available data. From this distribution it was determined that the maximum Cu concentration at which *Melanotaenia nigrans* was observed to behave normally, and occur in abundance, in the EB in 1993 is equivalent to a concentration toxic to approximately 90% of species, as reported in the literature. The maximum concentration at which *Mogurnda mogurnda* occurred was least for the five species and was equivalent to a concentration toxic to approximately 20% of species reported in the literature.

The presence of *Melanotaenia nigrans* in abundance in the East Branch indicates that its populations may have acquired tolerance to these contaminant levels. Such tolerance may be attributable to their long period of exposure to elevated levels, that were previously observed to cause death and may be operating as a mechanism to select those individuals in the populations that are genetically pre-disposed for tolerance to mine-waste contaminants (Mulvey and Diamond 1991).

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Reducing Impacts to Ecosystems During Contaminated Site Remediation – Recent Experience on Setting Targets and Selecting Remediation Technologies

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ABSTRACT: A wide variety of remediation technologies are now available to deal with a range of impacts to soil and groundwater. However, while there are obvious environmental benefits of these technologies to the soil and groundwater, remediation activities can produce a range of environmental impacts to the wider ecosystem, including: wastes generated that require off-site disposal; energy consumption and associated greenhouse gas emissions; impacts to air quality; noise impacts; and other potential impacts. Recent case studies are discussed, including data regarding environmental impacts from a major site remediation. Remedial action plans developed and agreed with regulators and, in some instances, local community consultation groups, have resulted in a more holistic approach to setting remediation targets and selecting remediation technologies. These approaches include setting targets on a site specific basis, a more long-term approach to managing soil and groundwater impacts, and reducing impacts to the wider ecosystem.

KEYWORDS: soil, groundwater, remediation, environmental impact

INTRODUCTION

This paper presents recent experience in reducing impacts to ecosystems during contaminated site remediation activities, and examples from several high profile sites that included consultation with both regulators and community groups. The sites are located within Victoria, Australia. There have been many technical and social developments, at a national and local level, relating to contaminated sites in recent years, including:

(a) Legislation and State Environment Protection Policies relating to soil and groundwater (Environment Protection Act 1970, Victoria Government Gazette 1997, EPAV 1998);

(b) Instigation of the Victorian Environmental Audit system under Section 57AA of the Environment Protection Act, 1970. To support this system, the Victorian Environment Protection Authority (EPAV) has also issued guidance notes to auditors and other documents relating to both technical and policy matters. Other national legislation has also been implemented (NEPC 1999); and,

(c) Raised public awareness of environmental issues, including those related to contaminated land and groundwater. In Victoria, there has also been considerable public debate regarding hazardous waste, which has resulted in formation by the Victorian government of a Hazardous Waste Consultative Committee. One of the roles of this committee was to provide advice on the development of a statutory industrial waste management policy in concert with EPAV. The committee produced a report in April 2000 (Hazardous Waste Consultative Committee 2000), which emphasised a reduced reliance on landfill for disposal of solid wastes.

There have been a number of implications arising out of these technical and social developments, including:

(a) from the technical viewpoint, there has been a greater focus in the use of risk assessments as opposed to generic "acceptance" criteria, a greater acceptance of risk management, and more extensive use of natural attenuation as a remediation option;
(b) there remains a requirement for the removal of non-aqueous phase liquid (Victoria Government Gazette 1997) unless EPAV "is satisfied that there is no unacceptable risk posed to any beneficial use by the non-aqueous phase liquid";
(c) there has been a greater involvement of community groups for major sites having soil and groundwater issues; and,
(d) there has been a greater awareness of the environmental impacts of active remediation systems to environmental aspects other than soil and groundwater.

In light of the above developments, this paper describes the development of remedial action plans in consultation with EPAV and, in some instances, with local community groups. A primary focus of these remedial action plans has been setting targets and selecting remediation technologies.

Environmental Benefits of Soil and Groundwater Remediation

The environmental benefits of performing soil and groundwater remediation are well documented, and are usually the driver for performing soil and groundwater remediation works. Benefits include:

(a) reduced risks to current or potential receptors, including humans, flora and fauna;
(b) reduced risk of damage to buildings or other infrastructure;
(c) restoration of an environmental resource, e.g. groundwater supply; and,
(d) compliance with environmental legislation or guidelines.

Environmental Impacts of Soil and Groundwater Remediation

The primary impacts associated with soil and groundwater remediation systems include:

(a) wastes generated that require off-site disposal (major sources of wastes include contaminated soils being removed to landfill, abstracted groundwater, and waste granulated activated carbon from off-gas treatment);
(b) energy consumption and associated greenhouse gas emissions (major contributors are gas / electricity consumed by *in situ* remediation systems - vacuum pumps, blowers, compressors, thermal treatment systems, off-gas treatment equipment);
(c) impacts to air quality by fugitive emissions during excavation and landfarming, or by emissions from remediation equipment such as vapour extraction systems;
(d) surface water and sediment run-off may be exacerbated by civil engineering works;
(e) noise impacts, especially to local residents, are a significant issue associated with both excavation and transport, and *in situ* remediation systems; and,
(f) other potential impacts such as vibration impacts to properties in the vicinity, possible impacts to the visual amenity of a site, potential Legionella issues associated with cooling towers and removal of vegetation during remediation work.

CASE STUDIES

Oil Terminal Remediation

The first case study concerns remediation of an operating oil terminal in Spotswood, Victoria currently operated by Mobil Oil Australia (Mobil). The site details and remedial system are summarised in Tables 1 and 2 respectively. Hydrocarbon removal is summarised in Fig. 1.

Table 1. Spotswood Oil Terminal, summary site details

Parameter	Description
Historical / current site use	Storage of petrochemical products for approximately 70 years
Site geology	Basaltic clays and fill to a depth of 0.5 – 3 m below ground level (mBGL) overlying basalt (Quaternary Newer Volcanic) to approximately 30 mBGL
Site hydrogeology	Standing water levels in regional groundwater of 7-12 mBGL with groundwater flow in a northeasterly direction. Some perched water, including backfilled quarries in the area
Contaminants	Primarily a mixture of petroleum hydrocarbons (lubricating oil, diesel, petroleum) with some solvents (including methyl ethyl ketone). Light nonaqueous phase liquid (LNAPL) present at up to 3.5 m apparent thickness and extending over an area of 7 ha. Some metal impacts to fill imported on the site, with isolated impacts to groundwater
Sensitive receptors	Primarily site workers, flora and fauna in Stony Creek 100 m to the north, and the Yarra River 600 m to the east. No evidence of LNAPL or dissolved-phase hydrocarbons discharging to these surface water bodies. No groundwater is currently extracted in the area for any beneficial use.

Table 2. Spotswood Oil Terminal, summary groundwater remediation details

Parameter	Description
Direct product removal	Product removal from an initial 11 down well skimmers from August 1994, phased out over initial 2 year period
Total fluids removal	Total fluids removal from an initial 30 top filling down hole pumps from August 1994. Maximum recovery 100 kL day^{-1}. Gradually reduced to 6 pumps (May 1999)
Vapour removal	Soil vapour extraction (SVE) from 15 extraction wells from December 1994. Removal rate approximately 1400 m^3 day^{-1}
Abstracted water treatment	Tilted plate separators, air stripping and settlement
Off-gas treatment	Thermal treatment in gas fired burner
Operation	Full time operation until Sept. 97. SVE only from Sept. 97 – Oct. 98. System shutdown from Oct. 98 – Jul. 99. Pulsed SVE operation and reduced groundwater abstraction since July 99.

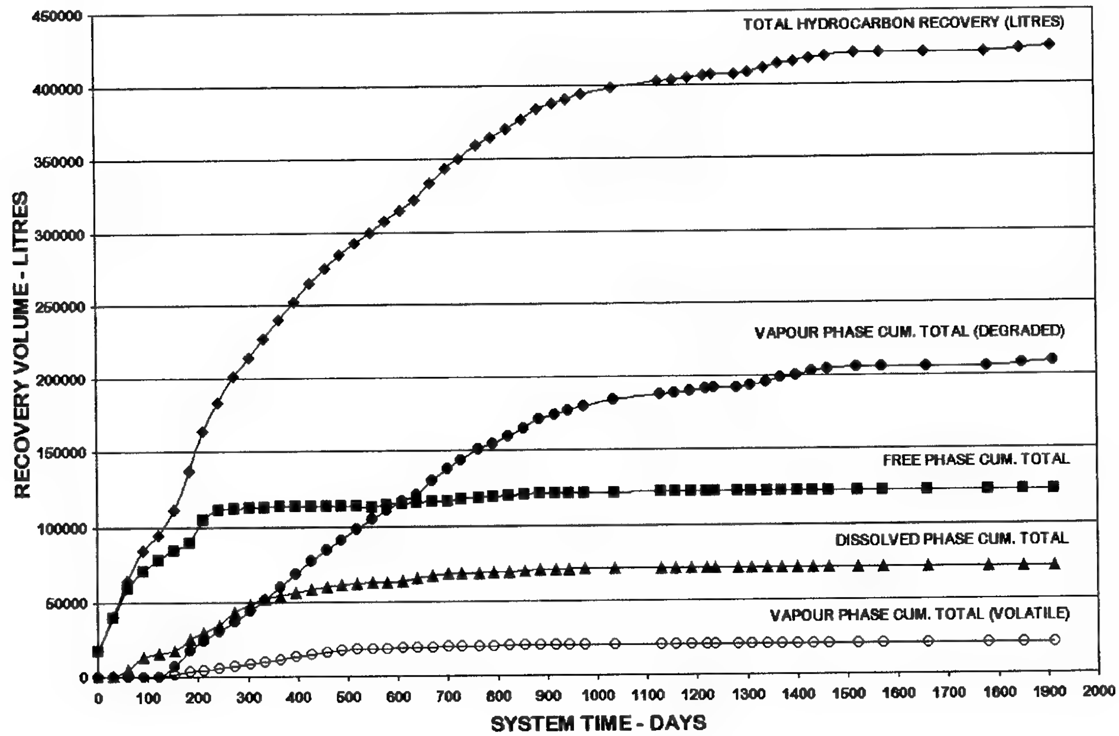

Fig. 1. Spotswood Oil Terminal, cumulative product removal

The environmental impacts of the active remediation system are summarised in Table 3. Greenhouse gas emissions from gas and electricity usage were based on data provided by the Australian Greenhouse Office (1998). It should be noted that Table 3 details only major impacts resulting from system operation, and excludes a number of impacts, including:

(a) any impacts relating to construction of the system, either in production of equipment or installation activities. Construction materials include over 10 t of steel and over 5 km of pipework;
(b) no allowance has been made regarding carbon dioxide generated by oxidation of contaminants. It is considered that all of the contaminants would eventually degrade naturally, and it is difficult to assess if short term oxidation of contaminants further to removal will result in a lesser or greater overall impact with regard to greenhouse gases; and,
(c) no allowance has been made for minor impacts, e.g. generation of office wastes.

It is also noted that as hydrocarbon removal rates have declined, the relative environmental impact per unit of hydrocarbon removed has increased. For example, the generation of carbon dioxide equivalents from gas and electricity usage has increased from 3.5 kg L^{-1} hydrocarbon recovered in 1994/1995 to 59 kg L^{-1} in 1999. Similarly, wastewater generated has increased from 90 L L^{-1} hydrocarbon recovered in 1994/1995 to 260 L L^{-1} in 1999.

Table 3. Spotswood Oil Terminal, Major Environmental Impacts from System Operations

Impact	Description
Wastes removed	56000 L product 1000 L biological sludge from settlement tanks 570 ML of treated groundwater to sewer
Greenhouse gases	191000 kg CO_2 equivalents from gas usage 15000 kg CO_2 equivalents from electricity usage
Air quality	Minor impacts. Point discharge within licence requirements, minor fugitive emissions
Noise impacts	Minor
Other impacts	Cooling tower operated with biocide dosing until 1997 (minor Legionella risk), other environmental impacts minor

The results demonstrate that active soil and groundwater remediation has an impact upon other aspects of the environment. Furthermore, it is usual for remediation rates to decrease with time in contracts of this nature, and the relative environmental impact per unit of contaminant treated increases.

Remediation targets are currently being developed with EPAV based on the following:

(a) active remediation is being targetted on areas with the most LNAPL;

(b) performance targets will be developed for active remediation, beyond which more passive methods will be used (e.g. skimmers, monitored natural attenuation);

(c) risk-based remediation targets will be developed for the site, protective of human health and groundwater receptors; and,

(d) passive remediation and monitoring will continue until risk-based targets have been met.

Chemical Manufacturing Site Remediation

The second case study concerns a polyvinyl chloride (PVC) manufacturing facility located at the Altona Chemical Complex in Victoria, and currently operated by Australian Vinyls (AV). The site details and remedial system are summarised in Table 4.

Table 4. Australian Vinyls Altona, Summary Site Details

Parameter	Description
Historical / current site use	PVC manufacture since 1960s, previously agricultural land. Until 1978, PVC manufactured from vinyl chloride monomer (VCM) generated by 'cracking' 1,2-dichloroethane (EDC). After 1978, PVC manufactured from polymerisation of VCM imported by roadtanker
Site geology	Basaltic clays to a depth of 0.5 – 2 mBGL overlying basalt (Quaternary Newer Volcanic) to approximately 40 mBGL
Site hydrogeology	Standing water levels in regional groundwater of 5-11 mBGL with groundwater flow in a south or southeasterly direction.
Contaminants	Primarily EDC. Lesser concentrations of other contaminants including other chlorinated solvents, petroleum hydrocarbons, polyaromatic hydrocarbons and metals
Sensitive receptors	Primarily site workers. Nearest identified groundwater body into which groundwater discharges is approximately 3.5 km to the south of the site

The following observations are noted regarding the plume behaviour and identified sensitive receptors.

(a) The EDC plume extends for approximately 500m to the south of the AV site, but appears to be contained within the Altona Chemical Complex.
(b) The plume appears to be stable, with no significant migration since extensive monitoring commenced in 1997. There are also geochemical indicators consistent with natural attenuation of EDC.
(c) EDC is a dense nonaqueous phase liquid (DNAPL). However, EDC concentrations appear to decrease with depth, presumably due to adsorption within clay layers observed within the basalt bedrock.
(d) A former tar storage area, identified as having shallow soil impacts, is currently fenced and is not routinely accessed by site personnel.
(e) The groundwater underlying the site is relatively saline (approximately 4000 – 5000 mg L^{-1} total dissolved solids, TDS). Potential beneficial uses include stock watering, industrial use and recreational use (e.g. abstraction for swimming pool water). However, the plume underlies a major chemical manufacturing facility and subsequent disposal of abstracted water to sewer would be limited by the high TDS. There is currently no abstraction of groundwater on the Altona Chemical Complex and the identified potential beneficial uses are considered unlikely.
(f) In view of the stable nature of the plume, it is considered unlikely that the contamination will impact upon any existing groundwater receptors in overlying aquifers (e.g. abstraction wells to the south of the site, Port Philip Bay).
(g) Risk assessment studies previously performed (ChemRisk Group and McLaren Hart Environmental Engineering 1995, EVS Environment Consultants 1997) suggest that risks to human health or environmental receptors from the groundwater contaminants were acceptable.

In summary, previous site operations have impacted upon certain potential beneficial uses of groundwater beneath the Altona Chemical Complex. However, these potential beneficial uses are considered unlikely. The groundwater is not considered to pose an unacceptable risk to human or environmental receptors.

A community consultation group, including EPAV and local residents, has considered groundwater issues related to the Australian Vinyls site. Treatment options were assessed against the following assessment factors agreed by the community group:

(a) 'net environmental benefit', a subjective assessment taking into account environmental impacts such as discharges to the environment, including off-site disposal, generation of greenhouse gases and resources required (e.g. power);
(b) efficacy of the treatment regarding: removal of free product; limiting off-site migration of contaminants; limiting migration of the entire plume and improving beneficial use of off-site groundwater already impacted;
(c) certainty that the remedial technology was technically feasible;
(d) certainty that the technology could be licensed to operate;
(e) likely operation time;
(f) costs.

The following treatment strategy was adopted in consultation with the community group.

(a) Source zones were identified on the Australian Vinyls site with highly raised concentrations of chlorinated solvents, probably indicative of DNAPLs in the vicinity. Source zones include shallow basaltic clays, basalt above standing water levels and groundwater.

(b) Australian Vinyls has committed to treat the source zones. It was recognised that technologies required for the treatment were in development or unproven, and the heterogeneity of the site would make uniform and complete treatment impractical.
(c) Treatment targets would be subject to further assessment of what was practical and consideration of the environmental costs and benefits of continued operation.
(d) Groundwater outside the source zone would be treated by natural attenuation, and a monitoring programme would be implemented to assess long-term plume trends and highlight any unexpected developments.
(e) Where possible, all wastes would be treated on-site and discharges would be compliant with regulatory requirements.

The following methodology was proposed to meet the above strategy.
(a) Chlorinated solvents would be removed from groundwater and vadose source zones by a combined air sparging / soil vapour extraction system. Groundwater pumping was not selected as the naturally elevated TDS values made water disposal difficult and may have affected contamination migration on other sites within the Altona Chemical Complex.
(b) Off-gas treatment would be by catalytic oxidation followed by caustic scrubbing of hydrogen chloride generated by the oxidation process. Catalytic oxidation at 450 – 490°C would minimise the generation of polychlorinated dibenzo dioxins and polychlorinated dibenzo furans that may occur at higher temperatures (notably at 750 – 900°C).
(c) Scrubber effluent containing sodium chloride would be disposed to sewer under a City West Water Trade Waste Agreement.

CONCLUSIONS

It is obvious that active remediation of soil and groundwater may result in impacts to other aspects of the environment. Therefore, proposed remedial action plans need to be developed considering environmental impacts and benefits of the proposed remediation, as well as factors such as compliance with legislation, the technical efficacy of the proposed remediation methods, costs, and timescale required for remediation targets to be attained.

The following conclusions are made with regard to selecting remediation technologies and setting remediation targets.

(a) Where passive remediation options are available, active remediation technologies should only be used where factors such as risks to human health or the environment, or compliance with environmental legislation, outweigh the environmental impacts of the remediation. In these circumstances, treatment efficiency will probably decrease with time, resulting in increased environmental impacts per unit of contaminant removed. Contaminant removal rates should therefore be considered when determining when active remediation should cease.
(b) The above decisions may involve subjective and policy judgements, in addition to technical considerations, and may require consultation with regulatory bodies and the local community.
(c) Active remediation, or if applicable passive remediation / monitored natural attenuation, should continue until risk-based remediation targets have been attained. Risk-based remediation targets should consider likely beneficial uses of soil and groundwater.

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Natural Attenuation of Hydrocarbons Leaching from a Fuel Depot into a Creek Ecosystem

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ABSTRACT: Investigations at a country fuel depot indicate areas of separate phase hydrocarbons floating on the groundwater surface. Recovery of the separate phase diesel and gasoline has indicated that natural attenuation of the contaminants accelerates quickly with source removal. An adjoining ephemeral creek has also been monitored for potential impact. The results have shown that the concentration of contaminants at the depot exceeded Australia's accepted criteria for maintaining river health. However, the concentrations of the contaminants decreased with increasing distance towards an unnamed tributary of the Yass River. In conclusion, the available data indicate that the receiving environment has sufficient distance between the source zone and receiving aquatic ecosystem to ensure adequate protection of riverine health. Further, the use of inappropriate ecological contaminant guidelines may result in remediation activities which do not reflect the site-specific risks to human health and the environment.

KEYWORDS: natural attenuation, remediation, ecosystem, benthic, pelagic

INTRODUCTION

Recently the Australian and New Zealand Environment and Conservation Council (ANZECC) released their draft guidelines for protecting fresh and marine water quality (ANZECC 1999). The objective of these guidelines was:

"to provide an authoritative guide for setting water quality objectives required to sustain current, or likely future, environmental values for natural and semi-natural water resources in Australia and New Zealand".

The current ANZECC guidelines (1992) adopted by catchment managers in Australia to date are soon to be replaced by these draft guidelines. The new guidelines recognise that aquatic ecosystems are highly diverse and complex systems that often require at least catchment-specific management strategies and may even require species-specific strategies in order to determine appropriate limits on polluters. A common problem with the 1992 ANZECC guidelines is their inherent lack of site-specific data, which has resulted in some catchment managers setting unrealistic requirements on stakeholders that pollute. In other instances the guidelines are inappropriate for maintaining the health of certain instream fauna.

Environmental investigations at a country fuel depot, which has operated since the 1920s, indicate areas of phase separate hydrocarbons (PSH) floating on the groundwater surface. A detailed assessment program of over 60 monitoring wells has defined the plume dynamics of the largely diesel and gasoline contamination. There are five known contaminant sources, with reported spills or leaks occurring since 1977. Subsequently, an active recovery system was installed including, active and passive PSH recovery and the pumping of groundwater through an oil/water separator and air stripper.

The depot is bounded by residential and commercial properties, a railway line, rural land and a main road. Sensitive receptors located within the vicinity of the depot include: residential properties to the north; an irrigation bore to the south; and an ephemeral creek (approximately 40 m from the depot boundary) to the west of the depot leading into the Yass River system approximately 150 m from the depot boundary. The ephemeral creek is the most ecologically sensitive of these receptors. This is because it is the ultimate receiving point for groundwater and because it provides habitat for some of the local aquatic invertebrates and frogs. The invertebrates and frogs would be directly effected by fluctuations in water quality, as they require water for respiration and for foraging. The catchment between the depot and receiving creek is characterised by introduced and native grasses, some of which are used for grazing by cattle and local native fauna. These animals are also potential receptors of surface and groundwater pollutants, however, they would be secondary receivers via their food and potential drinking water source.

The fuel depot is located on an elevated knoll with a groundwater mound existing at the centre of the site. The groundwater flow radiates from the site with the overall subsurface flow towards the Yass River, via the ephemeral creek located to the west of the site (Fig. 1).

The depot is underlain by surface clays to a depth of 1 m, followed by clayey sand to a depth of approximately 6 m. Underlying the sand is a high-level alluvial coarse quartz sand/gravel, overlying sandstone at a depth of approximately 7 m.

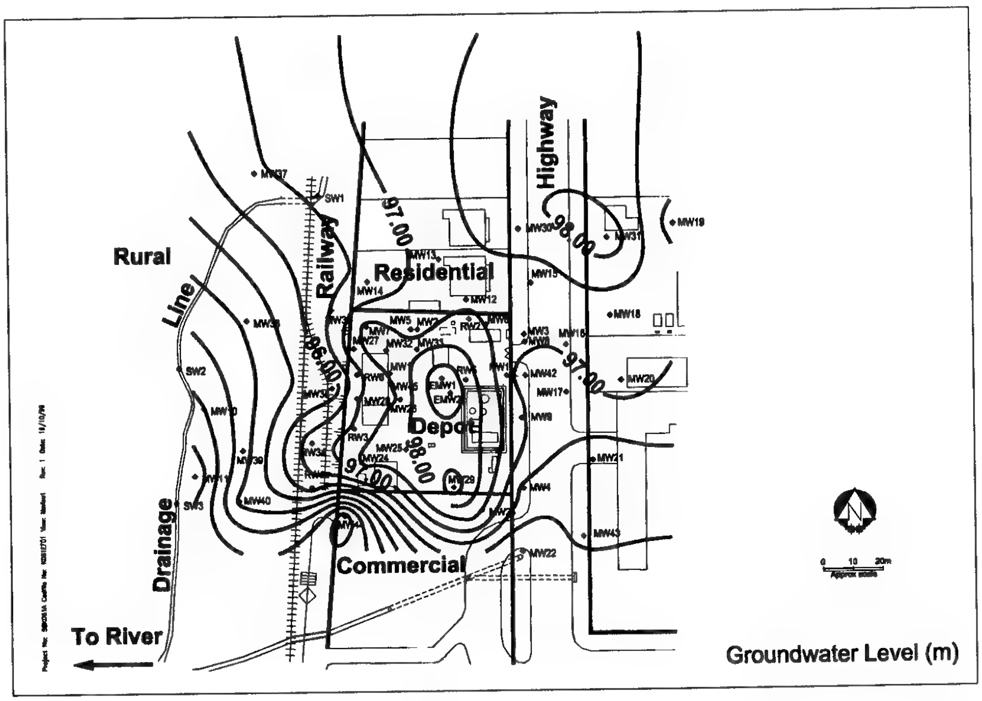

Fig. 1. Site plan and groundwater elevation contours

FIELD AND LABORATORY STUDIES

Monitoring of the groundwater has been undertaken since 1995 generally on a three-monthly basis, with the most recent groundwater sampling undertaken during June 2000. Surface water from the ephemeral creek was first sampled during January 1999. The aim of the monitoring program was to determine the extent and movement of a hydrocarbon plume

generated from the fuel depot. Monitoring has involved field gauging of apparent product (PSH) thickness, groundwater levels and field water quality parameters (temperature, pH, dissolved oxygen, redox potential and electrical conductivity). The groundwater samples were analysed at a NATA registered laboratory for polycyclic aromatic hydrocarbons (PAHs), monoaromatic hydrocarbons (BTEX compounds benzene, toluene, ethyl benzene and total xylene), total petroleum hydrocarbons (TPH) and indicators of natural attenuation (methane, ferrous iron, nitrate and sulphate). The ponds within the ephemeral creek system were also inspected for plant and animal life.

All groundwater monitoring wells were gauged with an interface probe to calculate the product thickness, if present, and depth to groundwater. Sampling of groundwater was undertaken at selected key monitoring wells both on and off-site, these monitoring wells were chosen based on their location and past results.

Surface water samples were collected from seven locations, both up and down gradient of the depot along the ephemeral creek. These samples were collected within pools of water along the creek. Visual inspections for plant and animal life within the pools was also undertaken during the sampling.

RESULTS

Evidence provided by regular sampling and analysis indicated that the petroleum hydrocarbons at the depot have a natural half-life of approximately 0.6 years (Dale *et al.* 1999). Hydraulic conductivity tested at the site varied from between 0.05 to 0.3 m day^{-1}. The higher value of 0.3 m day^{-1} was likely to be have been influenced by the presence of fill material in a former tankpit. The average hydraulic conductivity across the depot would be lower. The low hydraulic conductivity at the depot can be attributed to the clay material to a depth of 6 m. Further, the presence of concrete over the majority of the depot reduces the direct infiltration to the underlying aquifer.

The results showed that the petroleum hydrocarbons in groundwater decreased in concentration with distance from the primary source. At the depot, the concentrations of the analytes tested in groundwater were found to be above the surface water trigger values set by ANZECC (1992). However, at the receiving creek, the analyte levels were found to be well below the ANZECC (1992) trigger values. The decrease in mean concentrations of petroleum compounds is shown in Fig. 2. This supports the evidence collected by Rice *et al.* (1997) which indicated that 90% of historical benzene plumes in California were less than 80 m in length and Australian data collected by Wright *et al.* (1999).

Evidence of natural attenuation at the depot included: a stable dissolved phase hydrocarbon plume; an overall reduction in the level of groundwater nutrients (nitrate and sulphate) and dissolved oxygen; and an increase in levels of remediation by-products (such as methane and ferrous iron).

The results of the analysis undertaken on the indicators of natural attenuation showed that:

(a) the concentration of nitrate increased with distance downstream of the primary source;
(b) the concentration of sulphate increased with distance downstream of the primary source;
(c) the concentration of methane decreased with distance downstream of the primary source;
(d) the concentration of ferrous iron remained relatively stable, with an overall decrease in concentration with distance downstream of the primary source; and

(e) the concentration of dissolved oxygen increased with distance from the primary source.

The results of the analysis were in accordance with that expected of a system undergoing natural attenuation within the source areas (Landmeyer *et al.* 1998 and Walt and McNab 1997).

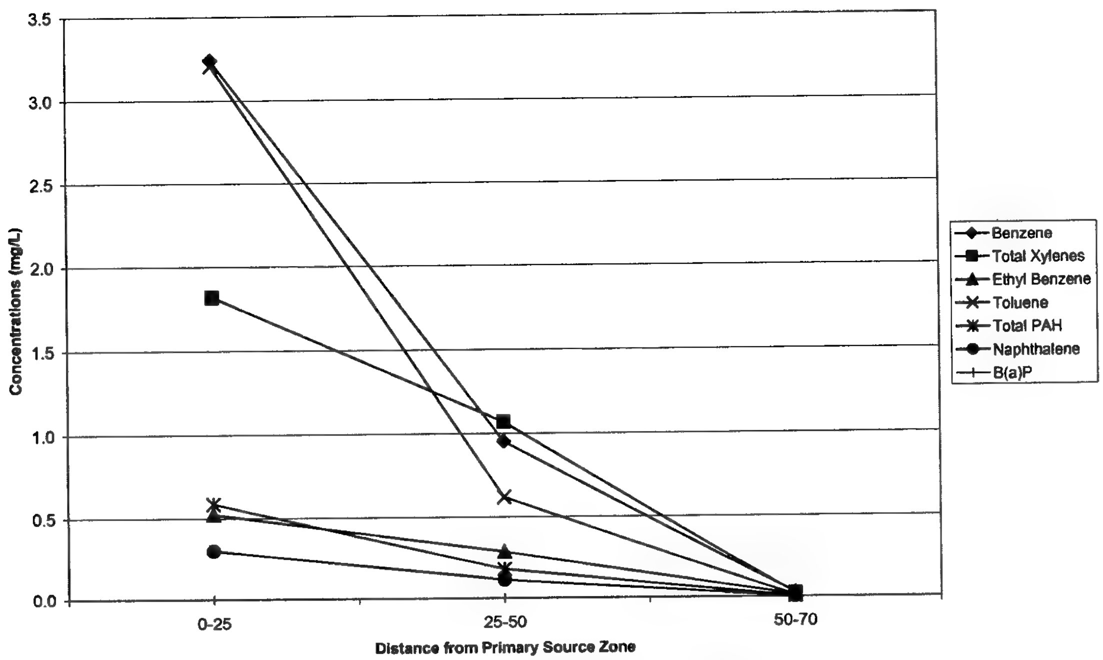

Fig. 2. Mean concentrations of petroleum hydrocarbons versus distant from source zone

The literature search on freshwater biota and the toxicity of petrochemicals showed that little relevant information was available. However, a comparison was made between the concentrations of toluene and naphthalene at the depot with toxicity data obtained from a paper by Cushman and Goyert (1984). The mean concentration of toluene found in the creek was 0.01 mg L^{-1}. This concentration is considered to be low in terms of biological sensitivity as indicated by previous 48-h LC_{50} assessments (acute toxic response) which have achieved results of greater than 50 mg L^{-1} for the benthic Dipteran, *Chironomus tentans* (Cushman and Goyert 1984). A Dipteran was used as a bioindicator because they normally show a high degree of sensitivity to oil contamination (Cushman and Goyert 1984).

The mean concentration of naphthalene found in the creek was 0.002 mg L^{-1}. This concentration is also considered to be low in terms of biological sensitivity as indicated by previous 48-h LC_{50} assessments which achieved results of around 3.29 mg L^{-1} for the benthic invertebrate *Chironomus tentans* (Cushman and Goyert 1984).

DISCUSSION

There is little knowledge of the effects of dissolved hydrocarbon contamination on freshwater ecosystems particularly with regards to the Australian condition. Existing literature on petrochemical pollution focuses on marine ecosystems. The current surface water criteria for PAHs (ANZECC 1992) is 0.003 mg L^{-1} is based on the 24-h LC_{50} of trimethylnaphthalene in the marine/estuarine copepod *Eurytemora affinis* (Ott *et al.* 1978 in

AWRC 1984). AWRC (1984) also note that this criterion should be used with caution because of the limited toxicity data on which it is based.

Published works favour larger catastrophic oil spills that do not necessarily display chronic responses by aquatic organisms. Further, work undertaken to date largely focuses on impact/response of aquatic ecosystems rather than on the dose response relationship of ecosystems (or components of ecosystems such as species specific data) and increased concentration of petrochemical pollutants. Finally there is little information on the pressure impacts of long term petrochemical discharges into freshwater ecosystems.

The effects of petrochemicals entering aquatic ecosystems are diverse and widespread, potentially effecting all macroinvertebrates in the aquatic food chain (Crunkilton and Duchrow 1990). They are largely dependent on the physical dispersal of the pollutant throughout the water column (Crunkilton and Duchrow 1990).

When petrochemicals reach water bodies, the volatile substances escape quickly and the soluble fractions slowly enter the water column (Crunkilton and Duchrow 1990). The dissolved fraction appears to be the most readily available to aquatic biota (Gagnon and Holdway 2000). At this stage the pollutants are made available to the pelagic species that are usually the larger and more mobile organisms inhabiting aquatic ecosystems (such as fish and amphibians). The pollutants are made available to these species via the gills, the digestive system and, in the case of some amphibians such as frogs, directly through their skin. Often the impacts of water pollution can be averted by pelagic species as they are more mobile and therefore can migrate away from the hydrocarbon plume. However, if the pollution becomes a longer term issue as a result of continual contamination over time, the impacts can have greater significance to pelagic species as the contamination is not allowed to attenuate and/or the plume (if it is large enough) can spread over an area greater than their migratory range.

In addition to the volatile substances, petrochemical runoff also includes an insoluble fraction that floats or combines with particulate organic matter, ultimately sinking to the bottom where chemical and bacterial degradation may occur over time (Crunkilton and Duchrow 1990). At this stage, the pollutants are made available to benthic ecosystems effecting organisms such as insects, molluscs, crustaceans and annelids. This form of contamination is usually more long-term and the effects are hence chronic. These species are usually less mobile and therefore unable to migrate to areas of lower contamination.

The direct effects of petrochemical uptake by aquatic organisms includes:

(a) limitation of oxygen exchange;
(b) coating of gills of aquatic organisms;
(c) interference with respiration;
(d) pathological lesions on respiratory surfaces; and
(e) bioaccumulation of hydrocarbons (Crunkilton and Duchrow 1990).

Additional indirect impacts of petrochemical pollution involve a reduction in the decomposition rate of vascular plant litter, nutrient release from sediments and algal primary production, which can result in toxic blue-green algal blooms. Decomposition of oil may produce additional toxic effects through the consumption of oxygen. Both these impacts can result in fish kills.

It is widely accepted that pollution of aquatic ecosystems with petrochemicals results in an overall decrease in mean species diversity (Cushman and Goyert 1984). Recovery of aquatic biota from petrochemical pollution may be slow and the effects of a large spill can sometimes be devastating and may extend over a long period of time (Crunkilton and Duchrow 1990).

The impacts occurring at Yass involve longer term pressure relationships that would show chronic responses by resident organisms. It is expected that the results of contamination

such as this would be reductions in abundances of the more sensitive organisms as well as a reduction in overall species diversity. This reduction in overall diversity cannot, however, be divorced from the other urban impacts from runoff from a major roadway or other anthropogenic contaminant sources such as leaching from back yards or sewers (nutrients, hydrocarbons/greases, metals, salinity) which all reduce water quality without rigorous and often expensive experimental design using control sites and obtaining before and after samples.

The efficiency of natural attenuation at limiting contaminant migration in groundwater systems can be assessed by comparing rates of contaminant transport with rates of biodegradation (Landmeyer *et al.* 1998). As hydraulic conductivity of groundwater at the depot was relatively low, contaminant migration would be confined and would be less likely to reach sensitive receptors, such as the aquatic biota. Guidelines prepared by the American Society for Testing and Materials (1998) and past work undertaken by Landmeyer *et al.* (1998) and Walt and McNab (1997) suggest that the natural attenuation process is occurring within the source areas resulting in an overall decrease in concentration of petroleum hydrocarbons with increasing distance.

CONCLUSIONS

Although concentrations of petroleum hydrocarbons within groundwater at the depot are above guideline levels, these concentrations fall well below recommended levels within samples obtained from the instream biota. This reduction in hydrocarbons can be attributed to the process of natural attenuation. Natural attenuation appears to be adequately reducing contaminant levels such that the impacts on the creek are minimal. The 1999 draft ANZECC Fresh and Marine Water Quality Guidelines (which applies to surface water not groundwater) suggest that the guideline trigger levels contained therein provide an indication of preferred water chemistry required to maintain ecological values rather than a strict level for catchment managers to enforce. However, they also state that the guidelines provided could be modified to tailor for specific sites or regions.

Existing ecotoxicological information on Australian aquatic biota however is extremely limited and the study involved extrapolation between overseas data to the Australian experience. Without detailed studies of local bioindicators and their sensitivity to anthropogenic substances, the use of limited international studies can result in significant cleanup costs to ensure compliance with inappropriate standards.

While toxicity assessments for individual analytes can give an estimate of the acute and/or chronic effects of particular pollutants, they do not represent the potential synergistic toxicity that can occur in a natural system where other chemicals are readily available (Cushman and Goyert 1984).

It is important that catchment managers maintain a conservative approach to catchment management to ensure that a precautionary approach is maintained. However, guidelines for water body chemical parameters should be treated by catchment managers as guidelines and not as critical indicators of pollution. Furthering site-specific scientific knowledge of waterway biology and chemistry should set the triggers for anthropogenic contamination of aquatic ecosystems so that pollution impacts can be separated from the site-specific characteristics of individual water bodies. The use of catchment management and site-specific risk assessment should drive the need for risk-based remediation to provide cost effective solutions to urban contamination.

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Ecotoxicity of Copper, Chromium and Arsenic to Soil Flora and Fauna

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ABSTRACT: Ecotoxicity data is used for assessing chemical hazard, in ecological risk assessment at contaminated sites, and for monitoring the progress of remediation and mitigation activities to restore environmental health. Compared to aquatic toxicology, relatively few standardised testing procedures are available for assessing soil contaminants. Consequently, toxicity data for terrestrial organisms are sparse. In New Zealand, through the implementation of the Hazardous Substances and New Organisms Act (1996) and the Resource Management Act (1991), there is an increasing onus both to assess the potential hazards of contaminants and to determine the risks of adverse health effects arising from contamination. For some contaminants, soil quality criteria in New Zealand have been derived. However, emphasis is on the protection of human health, with token regard for potential ecological impacts. This paper describes the methodologies employed to test for impacts of three common metal contaminants on a range of soil invertebrates and plants.

KEYWORDS: ecotoxicity, soil quality criteria, copper, chromium, arsenic

INTRODUCTION

The relatively young discipline of ecotoxicology has arisen from the necessity to assess, monitor, and mitigate the impacts of progressively increasing quantities of contamination in our environment. At contaminated sites, chemicals present in the soil, as well as in on-site and off-site water bodies, can adversely affect the ecosystem by interfering with the growth, reproduction, and survival of resident populations of organisms. In order to evaluate environmental impacts of these contaminants, it is essential that reliable techniques are available which can measure their ecotoxicity.

A number of guidelines have been developed by international environmental agencies like the Organisation for Economic Cooperation and Development (OECD), for the testing of toxic substances using biological assays. The data from these standardised tests are used in (a) the hazard assessment of chemicals, (b) ecological risk assessment and risk management, and (c) monitoring the progress of remediation and mitigation activities to improve environmental health. Research in ecotoxicology has historically been focussed on the aquatic environment, as water is considered to be where most contaminants are ultimately deposited. Therefore, testing procedures for aquatic contaminants are relatively well developed, and consequently there is a voluminous body of toxicity data available for aquatic organisms. Compared to water, soil has a greater capacity to retain environmental contaminants and, like sediments, can concentrate chemicals. The comparatively few guidelines written for the risk assessment of soil ecosystems are underdeveloped, and standardisation of the testing methodology has only been achieved in a few cases (van Straalen and van Gestel 1993). In order to address this inadequacy a '*Handbook of Soil Invertebrate Toxicity Tests*' has been developed under the auspices of the European Union research and development SECOFASE

project (Lokke and van Gestel 1998). This handbook outlines scientifically rigorous methodologies designed for the provision of toxicity data that is suitable for regulatory purposes.

Heavy metals are common soil contaminants. The wood processing industry, for example, uses chemicals such as copper chrome arsenate (CCA) to preserve timber. These chemicals can be toxic to living organisms and they are also highly persistent in the environment. In order to better protect ecological receptors at metal-contaminated sites, there is a need to derive toxicity benchmark values for soil contamination by these compounds. Toxicity benchmark values for copper, chromium, and arsenic have previously been published for use in the assessment of soil contaminants (Efroymson *et al.* 1997a,b) but the confidence in these values is often low due to a paucity of appropriate data. Therefore, there is a need for standardised testing procedures to be employed to ascertain the effects of these contaminants on organisms relevant to the New Zealand environment. This paper presents soil testing protocols, adapted from international guidelines, to provide New Zealand-specific toxicity data for the common pasture worm, the woodlouse, the native plant kaka beak, as well as lettuce and millet.

METHODS

Test Soil

A New Zealand Templeton silt loam (5% organic matter, pH = 6.2) was used for our plant, earthworm, and woodlouse tests, thus permitting standardisation of conditions across all three bioassays. A 'standard' soil was considered preferable to the 'artificial' soil recommended in the OECD guideline for earthworm tests (OECD 1984a) as it allowed extrapolation to the field, as well as being able to support the plant tests. This standard laboratory soil was field collected, air-dried and sieved through a 5 mm^2 sieve, and stored under cover.

Test soils were spiked with analytical grade $CuSO_4$, $Na_2Cr_2O_7$ (Cr VI) or As_2O_5 (As V). A range finder test using at least five concentrations of metal ion per kg of soil was initially conducted to determine the approximate toxicity of the metals. The definitive concentration range was then selected and the final concentration range used in each test is described in Tables 1-3.

Soil for the invertebrate tests was allowed to rest at 20°C for 1 week prior to the introduction of test organisms. For the plant tests, seeds were planted within 24 h of incorporation of the test compound, as specified in the OECD guidelines. Prior to the commencement of the exposure period, soil samples were taken for residue analysis.

Plant Test

To date, no one standard plant test has been universally adopted by testing agencies, although there are a few methodologies available, i.e. OECD 208, USEPA OPPTS 850-4100 and 850-4150, ASTM E1598-94 (OECD 1984b, USEPA 1996a,b, ASTM 1994). Some of these protocols require testing of substances at specified application rates and are thus directed towards the testing of plant protection products. Our plant tests were based on the OECD procedure (OECD 1984b), but incorporated many of the recommendations outlined in the ASTM guideline (ASTM 1994). Our plant bioassays assessed seedling emergence (germination), growth (shoot and root biomass, and root length) and survival. The species tested included the native New Zealand species kaka beak (*Clianthus puniceus*), millet

(*Panicum milliaceum*), and lettuce (*Lactuca sativa*). For the definitive exposures at least five concentrations were tested including a control, with six seeds per replicate and five replicates per concentration (30 seeds per concentration). To allow for sufficient growth of kaka beak seedlings, which were slower to germinate than either lettuce or millet, the test duration was 4 weeks compared to 2 weeks for the standard species.

Earthworm Test

A range of guidelines have been developed for testing the acute and chronic toxicity of chemicals to earthworms. Acute toxicity can be evaluated in a 14-day test using the OECD guideline (OECD 1984a), while potential long-term effects can be evaluated using the 8-week International Organisation for Standardization earthworm reproduction test (ISO 1998). The United States EPA has developed a similar guideline, OPPTS 850.6200 (USEPA 1996c) to evaluate toxicity of chemicals to earthworms. These international guidelines all utilise adults of the species *Eisenia fetida*, selected for their ease of production and maintenance in culture. This earthworm, however, is not a soil-dwelling species, and its occurrence in the wild is limited to sites rich in organic matter. Experts have recommended enhancing the ecological relevance of the standard earthworm test by using indigenous soil-dwelling species such as *Aporrectodea caliginosa*, but describe it as being difficult to breed and handle in the laboratory (Kula and Larink 1998). *Aporrectodea caliginosa* is the most common earthworm in New Zealand pastures and it inhabits the topsoil, thus making it a far more valuable test species than *E. fetida*. We have been breeding and maintaining this particular species under laboratory conditions with relative ease, therefore to improve ecological relevance our testing protocol has been adapted for use in *A. caliginosa*, with some fundamental improvements.

The OECD guideline suggests that tests are conducted with the test material dissolved onto a filter paper or in artificial soil, but we have found that *A. caliginosa* is unable to maintain good health under these conditions. Therefore, we used a natural soil, thus enhancing the ability to extrapolate these test results to New Zealand soils. Our earthworm bioassay is a modification of the international guidelines that runs for 28 days in order to determine the effects on growth and mortality.

For the definitive test there were at least five test concentrations including a control, with 10 earthworms per replicate and four replicates per concentration (40 earthworms per concentration). Sensitivity to chemical contamination varies with age, and juveniles are more sensitive to pollutants than adults (Lagadic and Cacquet 1998). Therefore the relative sensitivity of juvenile (between 1 and 3 months old, with no clitellum) and adult (4 – 6 months old, with clitellum) specimens as test organisms was also compared. Data were collected weekly to provide LC_{50} and EC_{50} values at these time points.

Woodlouse Test

Woodlice (*Porcellio scaber*) play a critical role in organic matter breakdown for decomposition and related processes that are essential to soil health. Standard woodlouse test methods use survival, growth, and reproduction as measured end-points to estimate the potential impact of contaminants. We have only developed the growth and survival tests in this species, as breeding occurs at specific times of the year, which makes the reproductive test somewhat less flexible for commercial purposes. Standardised guidelines for woodlouse tests are not available so we based our test methods on *P. scaber* methods outlined by Hornung *et al.* (1998). For the definitive test there were at least five test concentrations

including a control, with 10 woodlice per replicate and four replicates per concentration (40 woodlouse per concentration).

Statistical Analysis and Derivation of Ecotoxicity Values

No observable effect concentrations (NOEC) and lowest observable effect concentrations (LOEC) were calculated using one-way analysis of variance (ANOVA), and *post hoc* Dunnett's test at $P < 0.05$. To fit assumptions of normality for an ANOVA, percentage data was arcsin transformed. Square-root or natural log transformations were applied to other data where appropriate prior to analysis. Median lethal concentrations (LC_{50} values) were derived from probit analysis of the mortality data. Median effect concentrations (EC_{50} values) were derived using polynomial regression (first, second and third order) of square-root-transformed data.

RESULTS

The range-finder tests for earthworms indicated that growth was a far more sensitive parameter than mortality. Definitive test concentrations were therefore selected using growth as an end point, and lethality values (LC_{50}) were not derived from these tests, with the exception of arsenic. Due to considerable labour required for the assessment of plant growth parameters, definitive test concentrations were estimated from germination and survival results, and therefore seedling LC_{50} values were also not always effectively derived from these tests.

Copper proved to have a far greater effect on earthworms compared to plants or woodlice (Table 1). The EC_{50} for growth in *A. caliginosa* was between 70 and 90 mg Cu kg^{-1}. Woodlice were insensitive to copper with no effects on growth or mortality at 2400 mg Cu kg^{-1} for up to 4 weeks (Table 1). Effects on lettuce germination were evident at the highest test concentration (results not shown). Unfortunately, the LOECs and NOECs for plant growth were inadequately characterised by these exposures because significant impacts of copper occurred at the lowest test concentration (600 mg Cu kg^{-1}).

The earthworm, *A. caliginosa,* exposed to chromium (VI) exhibited LOEC values between 50 and 150 mg Cr kg^{-1} (Table 2). Woodlice demonstrated adverse effects at chromium concentrations greater than 300 mg kg^{-1} (Table 2), whereas terrestrial plants had a far higher sensitivity to chromium with LOEC values for growth parameters as low as 20 mg Cr kg^{-1} soil.

Arsenic (V) exposure inhibited the growth of juvenile *A. caliginosa* at EC_{50} values between 40 to 50 mg As kg^{-1} (Table 3). Conversely, earthworm survival was a much more resilient end point, with a derived LC_{50} value of around 550 mg kg^{-1}. Woodlice were more sensitive to arsenic (in terms of survival) than earthworms with LC_{50} values of between 200 and 250 mg As kg^{-1} (Table 3). Terrestrial plants also appeared to be relatively sensitive to arsenic in the soil with derived EC_{50} values for growth ranging from 47 to 114 mg As kg^{-1}.

DISCUSSION

These results describe terrestrial ecotoxicity values for copper, chromium and arsenic in a natural soil. A number of important issues are highlighted by this work. Firstly is that while *E. fetida* is not a soil-dwelling species, its sensitivity to chemicals is considered representative of other earthworm species and it remains the international number one test-earthworm species. While we agree that for consistency in ecotoxicity data a common test species is

Table 1. Ecotoxicity values for copper

Species	Life stage	Duration (days)	Conc. (mg kg^{-1})	End point	NOEC (mg kg^{-1})	LOEC (mg kg^{-1})	Effect conc. (mg kg^{-1})
Earthworm							
A. caliginosa	Adult	14	0-600	Growth	< 100	100	EC_{50} = 88
A. caliginosa	Adult	28	0-600	Growth	100	200	EC_{50} = 70
A. caliginosa	Juvenile	14	0-300	Growth	< 150	150	EC_{50} = 91
A. caliginosa	Juvenile	28	0-300	Growth	< 150	150	EC_{50} = 92
Woodlouse							
P. scaber	Juvenile	14 & 28	0-2400	Growth	2400	> 2400	No value
Lettuce							
L. sativa		14	0-2400	Root weight	< 600	600	EC_{50} = 379
L. sativa		14	0-2400	Root length	< 600	600	EC_{50} = 322
L. sativa		14	0-2400	Shoot weight	< 600	600	EC_{50} = 449
Millet							
P. millaceum		14	0-2400	Root weight	600	1200	EC_{50} = 1412
P. millaceum		14	0-2400	Root length	< 600	600	EC_{50} = 406
P. millaceum		14	0-2400	Shoot weight	600	1200	EC_{50} = 1382

Table 2. Ecotoxicity values for chromium

Species	Life stage	Duration (days)	Conc. (mg kg^{-1})	End point	NOEC (mg kg^{-1})	LOEC (mg kg^{-1})	Effect conc. (mg kg^{-1})
Earthworm							
A. caliginosa	Adult	14	0-400	Growth	< 150	150	EC_{50} = 80
A. caliginosa	Adult	28	0-400	Growth	**	**	**
A. caliginosa	Juvenile	14	0-400	Growth	< 50	50	EC_{50} = 235
A. caliginosa	Juvenile	28	0-400	Growth	50	100	EC_{50} = 252
Woodlouse							
P. scaber	Juvenile	14	0-600	Mortality	400	500	LC_{50} = 544
P. scaber	Juvenile	28	0-600	Mortality	300	400	LC_{50} = 428
Lettuce							
L. sativa		14	0-80	Time to emerge	20	40	No value
L. sativa		14	0-80	Germination	20	40	**
L. sativa		14	0-80	Root weight	< 20	20	EC_{50} = 15
L. sativa		14	0-80	Root length	20	40	EC_{50} = 29
L. sativa		14	0-80	Shoot weight	< 20	20	EC_{50} = 15
L. sativa		14	0-80	Mortality	60	80	LC_{50} = 50
Millet							
P. millaceum		14	0-80	Root weight	80	> 80	**
P. millaceum		14	0-80	Root length	40	60	EC_{50} = 72
P. millaceum		14	0-80	Shoot weight	40	60	EC_{50} = 68
Kakabeak							
C. puniceus		28	0-80	Root weight	< 20	20	EC_{50} = 55
C. puniceus		28	0-80	Root length	20	40	EC_{50} = 65
C. puniceus		28	0-80	Shoot weight	20	40	EC_{50} = 53
C. puniceus		28	0-80	Shoot weight	20	40	EC_{50} = 53

** EC_{50} not derived where toxicity curve was incomplete or did not follow a dose-response relationship.

Table 3. Ecotoxicity values for arsenic

Species	Life stage	Duration (days)	Conc. (mg kg^{-1})	End point	NOEC (mg kg^{-1})	LOEC (mg kg^{-1})	Effect conc. (mg kg^{-1})
Earthworm							
A. caliginosa	Adult	14	0-400	Growth	< 50	50	**
A. caliginosa	Adult	28	0-400	Growth	50	100	**
A. caliginosa	Juvenile	14	0-100	Growth	40	60	EC_{50} = 43
A. caliginosa	Juvenile	28	0-100	Growth	40	60	EC_{50} = 49
A. caliginosa	Juvenile	14	0-600	Mortality	400	600	LC_{50} = 552
A. caliginosa	Juvenile	28	0-600	Mortality	200	300	LC_{50} = 552
Woodlouse							
P. scaber	Juvenile	14	0-400	Mortality	200	300	LC_{50} = 207
P. scaber	Juvenile	28	0-400	Mortality	200	300	LC_{50} = 241
Lettuce							
L. sativa		14	0-400	Time to emerge	275	350	No value
L. sativa		14	0-200	Root weight	50	100	EC_{50} = 74
L. sativa		14	0-200	Root length	50	100	EC_{50} = 114
L. sativa		14	0-200	Shoot weight	25	50	EC_{50} = 61
L. sativa		14	0-200	Mortality	275	350	LC_{50} = 339
Millet							
P. millaceum		14	0-400	Time to emerge	100	200	No value
P. millaceum		14	0-400	Root weight	< 100	100	EC_{50} = 112
P. millaceum		14	0-400	Root length	< 100	100	EC_{50} = 69
P. millaceum		14	0-400	Shoot weight	< 100	100	EC_{50} = 47
P. millaceum		14	0-400	Mortality	350	400	**
P. millaceum		14	0-400	Mortality	350	400	**

** EC_{50} not derived where toxicity curve was incomplete or did not follow a dose-response relationship.

desirable, we believe that the results obtained for *A. caliginosa* are more relevant. Furthermore, our results clearly indicate that LC_{50} values derived for *E. fetida* can underestimate chemical impacts on *A. caliginosa*. For example, the EC_{50} of copper for *A. caliginosa* was 70-90 mg Cu kg^{-1}, which is much lower than that reported for *E. fetida,* which has an EC_{50} value of 600 mg Cu kg^{-1} (Spurgeon and Hopkin 1996). Furthermore, *A. caliginosa,* demonstrated a higher sensitivity to chromium (VI) with a LOEC value for adult earthworms of 150 mg Cr kg^{-1} (Table 2) compared with 625 mg Cr kg^{-1} for *E. fetida* over the same test duration (Molnar *et al.* 1989). These findings suggest that international data using *E. fetida* as the test species has some limitations for determining potential contaminant impacts on New Zealand soil invertebrates.

Secondly, it is a topic of debate amongst experts as to the preferred test media for soil ecotoxicity tests. Soil type can have a dramatic influence over the bioavailability of a contaminant. For example, soil pH can influence the form of a chemical and the presence of a high level of organic matter in soil can result in a high level of bonding with the contaminant. An artificial soil is recommended for use in soil toxicity tests so that results can be standardised across one set of conditions. While there is a lot of merit in this suggestion, it is very difficult to translate results generated from a synthetic soil for site-specific risk assessments. Our plant test results for copper toxicity in a silt loam soil are comparable to those reported for the cucumber *(Cumcumbia sativus)* in a sandy loam soil, where EC_{50} values for germination and growth were 1725 and 540 mg Cu kg^{-1}, respectively (Mitchell *et al.*

1988). However, the EC_{50} for lettuce germination in synthetic soil was at least 40-fold lower (Vaughan and Greenslade 1998). These results strongly suggest that the toxicity values obtained using synthetic soil can overestimate toxicity in a natural soil.

Mortality end points such as LC_{50} values are commonly used to predict toxicity of contaminants. However, our results support the general opinion that sublethal end points are more sensitive (compare the LC_{50} and EC_{50} values for arsenic toxicity in earthworms in Table 3), and may consequently be more useful for predicting the ecological consequences of low levels of exposure to a particular contaminant.

The soil guideline value for copper in soil at timber treatment sites in New Zealand is currently set at 130 mg kg^{-1} (MfE 1997). This level is expected to be protective of plant life and is similar to the benchmark value for plants of 100 mg kg^{-1} given in Efroymson *et al.* (1997a). Slightly lower values such as an investigation level of 63 or 91 mg kg^{-1} (depending on land use) are recommended for use in Canada (CCME 1997), and a benchmark value of 60 mg kg^{-1} has been derived for earthworms (Efroymson *et al.* 1997b). Our results demonstrated the lowest earthworm EC_{50} value for growth was at 70 mg kg^{-1}, suggesting that a further degree of conservatism on the 130 mg kg^{-1} value for copper might need to be considered for the protection of ecological receptors. The New Zealand soil quality criteria value for chromium (VI) is 25 mg kg^{-1} (MfE 1997). This concentration appears to be at the threshold for causing effects in plant species. Canada has lower guideline levels for investigation at 0.4 and 1.4 mg kg^{-1} (CCME 1997). In general, our ecotoxicity values confirm that the recommended guideline value for arsenic in New Zealand soils of between 10 and 20 mg kg^{-1} is appropriate for the protection of ecological receptors.

CONCLUSIONS

In conclusion, this paper gives some ecotoxicity values for soil invertebrates and plants that are relevant to the New Zealand environment. Continued development of standardised terrestrial testing protocols and generation of ecotoxicity data for environmental contaminants will contribute to a database necessary for the proper hazard assessment of soil contaminants to ecological receptors. The influence of soil type on resultant ecotoxicity values is of utmost importance and requires further investigation in order to improve ecological risk assessments at contaminated sites.

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Using Source to Ecosystem Modelling in Risk Assessment to Avoid an Ecological Restoration Becoming an Ecological Disaster

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ABSTRACT: A quantitative ecological risk assessment of an old orchard site revealed that through the creation of new habitats, several bird species may be exposed to unacceptable levels of DDT. Further assessment revealed that the positioning and type of habitats being created were critical factors that influenced the risk. Additionally, the creation of a more biologically productive environment that encourages birds to feed more substantially in the contaminated environment is shown to increase exposure and potentially increase risk. The creation of a wetland is also shown to potentially increase DDT exposure to some terrestrial birds through bioconcentration effects, and the contamination of drinking water. However, the presence or absence of the wetland was not shown to markedly affect the overall degree of ecological risk. The ecological risk assessment undertaken in this study was used to illustrate how the creation of a new habitat in a contaminated environment can open up exposure pathways and how an ecological restoration could potentially become an ecological disaster.

KEYWORDS: DDT, DDD, DDE, organochlorine pesticide, ecological risk assessment

INTRODUCTION

The Blackwood forest site is situated on 21.2 ha of hilly land in the Coromandel Valley, South Australia. It was established as an experimental orchard in 1908 and was used for nearly 60 years as an experimental orchard to test the effectiveness of various agricultural techniques, including the application of pesticides. Since its closure and removal of the fruit trees in 1968, the site has, with the exception of the open grassland (which has undergone seasonal cutting), been allowed to grow wild. Today the site consists of: 8 ha of open grass land; 8 ha of mature pine forest; and native, ornamental, orchard and pest vegetation that has established along the perimeter of the small ephemeral watercourse (Fig. 1). Together, these provide a rather degraded habitat in which a few species of birds and mammals that are predominantly pest species, reside.

The surrounding area consists of a native forest reserve, creeks and low to medium density housing that is substantially vegetated with eucalypts. As a result, the surrounding area provides a number of habitats for a range of fauna. In a strategy to increase species diversity and more effectively use the site, it was proposed to:

(a) restore the native river red gum and grey box gum;
(b) create two wetland habitats;
(c) create a native open grassland habitat and playing field; and
(d) develop a residential area to pay for the ecological restoration (Fig. 2).

However, when habitats are created that mobilise the contamination from the source into the ecosystem, ecological restoration can potentially turn into ecological disaster. The risk to birds associated with the creation of the new habitats has been assessed.

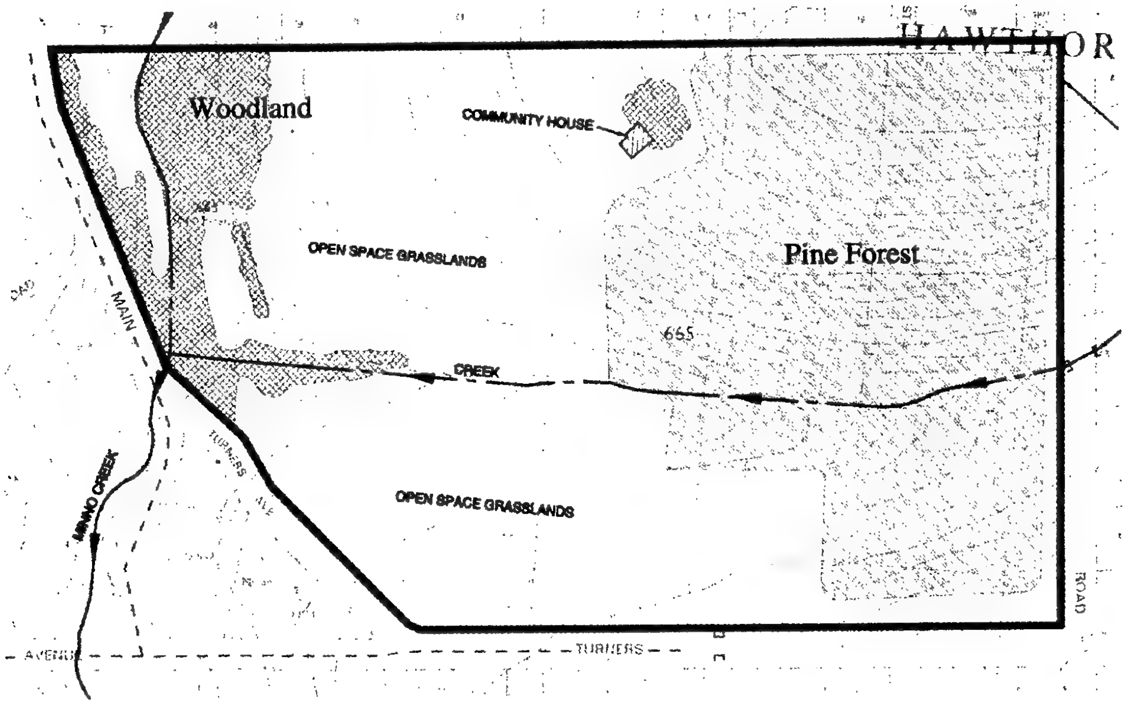

Fig. 1. Current land use environment

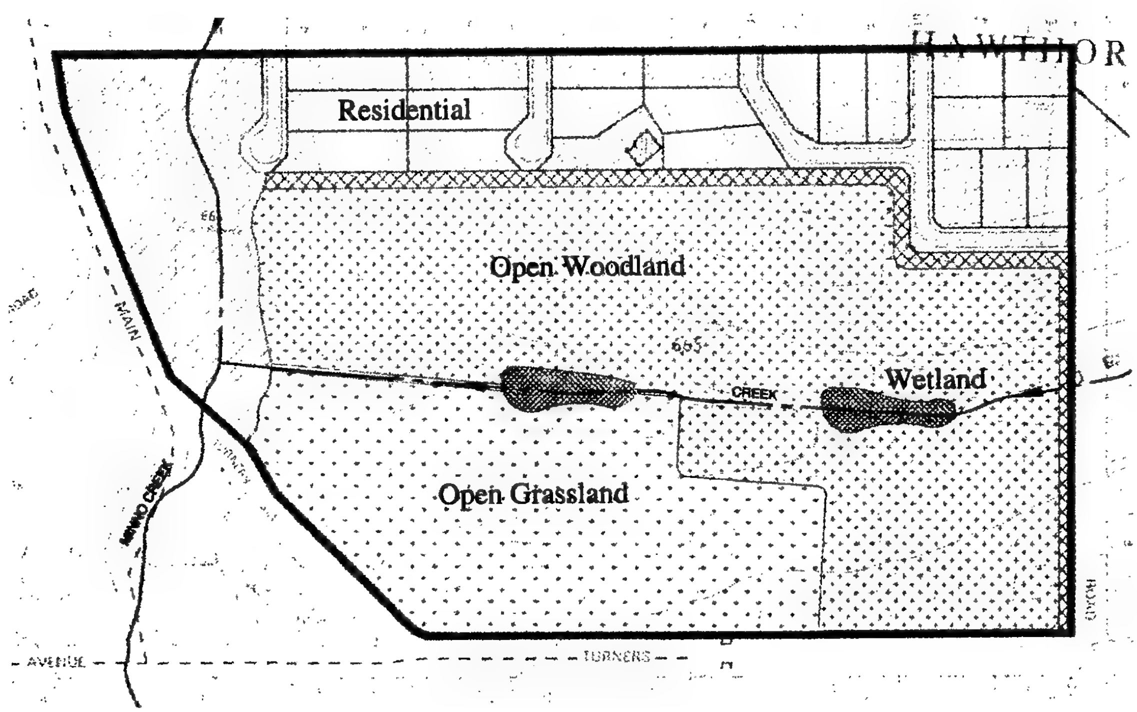

Fig. 2. Proposed land use environment with two wetland habitats

METHODS

To assess the potential risk posed by the creation of the new habitats to birds, the principles of ecological risk assessment (Walker *et al.* 1997a), which describe source to ecosystem modeling were applied.

The methodology used to evaluate risk qualitatively and quantitatively is consistent with the *National Environment Protection Measure (Assessment of Site Contamination)* (NEPC 1999). Risk is predicted using the equations described in, *Part B of the National Framework for Ecological Risk Assessment, NFERA-Part B* (EPAV 1996, Walker *et al.* 1997a,b). To account for foods with differing bioaccumulative potentials, protective soil concentrations (PSCs) have been derived using Eqn (1), a modified version of Equation 19 from the *NFERA–Part B.* Eqn 1. Equation (1) determines the predictive soil concentration, C prot. soil, from the exposure to a contaminant through the: ingestion of multiple foods with differing bioaccumulation potentials; soil ingestion; ingestion of drinking water; and the inhalation of air.

$$C_{prot.\ soil} = \frac{TTD * BW}{EF \left\{ SIR*B_{soil} + \Sigma(f_i * BF_i) * FIR*B_{food} + \frac{f_{aquatic}*FIR*BF_{aquatic}*B_{food} + WIR*B_{water} + AIR * B_{air} * H'}{K_{sw}} \right\}} \tag{1}$$

where, $B_{air,\ food,\ soil,\ water}$ is bioavailability for air, food soil or water; BF_I is bioaccumulation factor food type i ($mg_{toxin}\ kg^{-1}{}_{biota\ dry\ weight}\ /mg\ _{toxin}\ kg^{-1}{}_{soil\ dry\ weight}$); $BF_{aquatic}$ is bioaccumulation factor aquatic organism ($mg_{toxin}\ kg^{-1}{}_{biota\ dry\ weight}\ /mg\ _{toxin}\ L^{-1}{}_{water}$); BW is body weight ($kg_{wet\ weight}$); EF is exposure factor, i.e. the proportion of the life time spent at the site; FIR is food ingestion rate ($kg_{dry\ food}\ day^{-1}$); f_I is proportion of food that is of type i; $f_{aquatic}$ is proportion of food that is or has had an aquatic existence; H' is Henry's law constant ($L_{water}\ L^{-1}{}_{air}$); K_{sw} is soil water partition coefficient ($L\ kg^{-1}$); SIR is soil ingestion rate ($kg_{dry\ soil}\ day^{-1}$); AIR is air inhalation rate ($L_{air}\ day^{-1}$); TTD is total tolerable dose ($mg_{toxin}\ kg^{-1}{}_{body\ weight}$); WIR is water ingestion rate ($L_{water}\ day^{-1}$).

Risk is quantified in terms of a hazard quotient (HQ) for each relevant receptor. The HQ is derived from Eqn (2). The HQ is a ratio of the level of contamination at the site to the level of contamination that is not expected to impact on a specified organism:

$$HQ = C_{soil} / C_{prot.\ soil} \tag{2}$$

Where, C_{soil} is the mean soil concentration in a habitat ($mg\ kg^{-1}$).

It should be noted that while these levels are based on a best estimate or a most probable approach, there are numerous parameters that can not be accurately determined without site specific information. Where this is the case, the best estimate is made in terms of an approximation that guards against it being concluded that the level of contamination is acceptable when in fact it is not. As a result, the actual HQ for the described exposure scenario(s) is likely to be less than the calculated value. Therefore, HQs are reported as less than some number (i.e. < x) rather than a precise number. In addition to this, a HQ which may be greater than 1, indicates there is a raised probability that an impact may occur. This should not be interpreted that an impact will occur.

Considering this HQs are reported as:

(a) "<x" where x is any number less than or equal to 1, by definition describes the level of contamination as ***non-hazardous***;

(b) "<x" where x is any number less than or equal to 2 but greater than 1, by definition describes the level of contamination as ***probably non-hazardous***;

(c) "<x" where x is any number less than or equal to 5 but greater than 2, by definition describes the level of contamination as ***possibly non-hazardous***;

(d) "<x" where x is any number above 5, by definition describes the level of contamination as ***possibly hazardous***.

Therefore the risk in *Possibly hazardous* areas, may be greater than the risk in

(a) *Possibly non-hazardous* areas, which is greater than

(b) *Probably non-hazardous* areas, which is greater than

(c) *Non-hazardous* areas.

RESULTS

The theoretical level of contamination that may persist without presenting a hazard is referred to as the Protective Soil Concentration (PSC). The PSC for DDT for each species under the current, and proposed land use environment with and without a wetland habitat, is presented in Fig. 3. The species most tolerant of the contamination is the rainbow lorikeet. In the current land use environment this bird may withstand DDT soil concentrations in excess of 540 mg kg^{-1}. However in this same environment, the Australian magpie-lark is the most susceptible and may be impacted by DDT soil concentrations that are greater than 0.5 mg kg^{-1}. For a number of birds: the Australian magpie; Australian magpie-lark; grey currawong; and willie wagtail, the PSC in the current land use environment is higher than the proposed environments, indicating that these birds are able to tolerate a higher level of DDT contamination. For most birds the presence or absence of a wetland made little difference to the level of contamination they could tolerate. However, for the noisy minor, crimson rosella, red-browed fire-tail and willie wagtail the presence of a wetland decreased their individual PSCs, indicating the level of contamination that they could tolerate is significantly reduced.

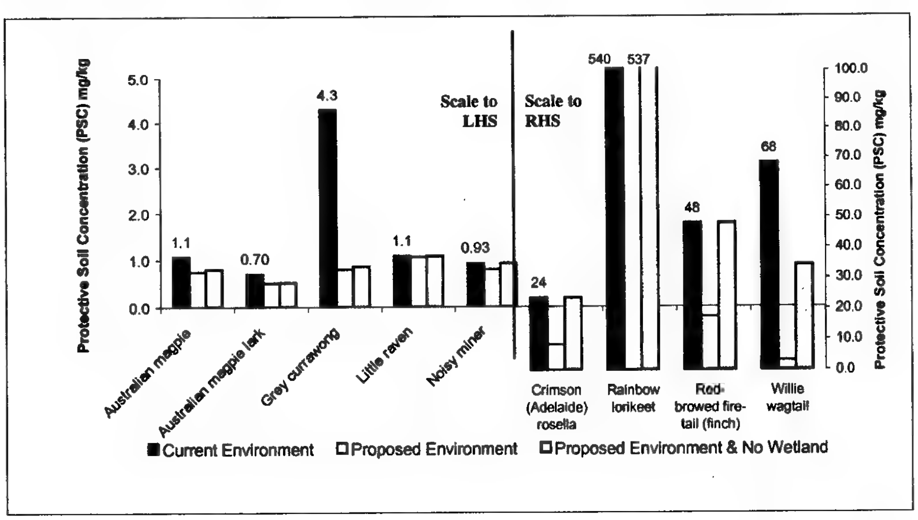

Fig. 3. Protective soil concentrations for birds in the current and proposed environments with a wetland and in the proposed environment without a wetland

The risk that is associated with the current land and proposed land uses and their terrestrial habitats are presented in Tables 1 and 2, respectively. Based on the mean DDT concentration across the site, the current and the proposed land use environments with and without wetlands are by definition:

(a) non-hazardous to five species (crimson rosella, grey currawong, rainbow lorikeet, red-browed fire-tail and willie wagtail);
(b) probably non-hazardous to three species (Australian magpie, little raven and noisy minor);
(c) possibly non-hazardous to one species, the Australian magpie-lark; and
(d) possibly hazardous to none of the species.

However, if species were to forage almost entirely in a single habitat, the risk to each may be substantially increased. In the current land use environment the open grassland habitat poses the highest risk with the contamination being possibly non-hazardous to 4 species and non-hazardous to 3. Similarly, the contamination in the open grassland environment of the proposed land use environments with and without a wetland, poses the greatest risk. In these environments the open grassland habitat is possibly hazardous to 1 species, possibly non-hazardous to 3 species and non-hazardous to 3 species.

Table 1. Hazard quotients for the habitats of the current land use environment based on chronic exposure and impact on reproduction

Bird	PSC >, (mg kg^{-1})	Hazard quotient (<) Current land use habitat: Open Grass.	Open Wood.	Pine Forest	Creek	Whole Site*
Australian magpie	1.07	3[b]	2[a]	5.E-01	2[a]	1.6[a]
Australian magpie lark	0.697	4[b]	2[a]	8.E-01	2[a]	2.5[b]
Crimson (Adelaide) rosella	23.5	1.E-01	7.E-02	2.E-02	7.E-02	7.E-02
Grey currawong	4.30	NRH	0.4	1.E-01	4.E-01	3.E-01
Little raven	1.08	3[b]	2[a]	5.E-01	1	1.6[a]
Noisy miner	0.927	3[b]	2[a]	6.E-01	2[a]	1.9[a]
Rainbow lorikeet	540	NRH	3.E-03	1.E-03	3.E-03	3.E-03
Red-browed fire-tail (finch)	47.9	6.E-02	4.E-02	1.E-02	3.E-02	4.E-02
Willie wagtail	68.3	4.E-02	2.E-02	8.E-03	2.E-02	3.E-02
		Mean habitat concentrations (mg kg^{-1})				
		2.77	1.68	0.54	1.61	1.75

*excludes relevant habitats; unmarked hazard quotient: Non-hazardous; [a]: Probably non–hazardous; [b]: Possibly non-hazardous; [c]: Possibly hazardous; N. Wet.: Proposed environment without the wetlands; NRH: Not a relevant habitat; Prop.: Proposed land use environment; Resi: Residential habitat.

Table 3. Hazard Quotients for the habitats of the proposed land use environments with and without a wetland habitat based on chronic exposure and impact on reproduction

			Hazard Quotient (<)									
	PSC >, (mg kg^{-1})		Proposed Landuse with Wetland				Proposed Landuse & No Wetland				Whole Site*	
Bird	Prop.	No Wet	Resi.	Open Grass.	Open Wood.	Creek	Resi.	Open Grass.	Open Wood.	Creek	Prop.	N. Wet.
Australian magpie	0.744	0.805	1	5^b	1	2^a		5^b	1	2^a	2.4^a	2.2^a
Australian magpie lark	0.504	0.523	2^a	8^c	2^a	3^b	2^a	7^c	2^a	3^b	3.5^b	3.3^b
Crimson (Adelaide) rosella	8.37	23.5	1.E-01	5.E-01	1.E-01	2.E-01	5.E-02	2.E-01	4.E-02	7.E-02	2.E-01	7.E-02
Grey currawong	0.797	0.861	1	NRH	1	2^a	1	NRH	1	2^a	1.4	1.3
Little raven	1.06	1.08	1	4^b	1	2^a	1	4^b	1	2^a	1.7^a	1.6^a
Noisy miner	0.796	0.927	1	5^b	1	2^a	1	4^b	1	2^a	2.2^a	1.9^a
Rainbow lorikeet	537	537	2.E-03	NRH	2.E-03	3.E-03	2.E-03	NRH	2.E-03	3.E-03	2.E-03	2.E-03
Red-browed fire-tail (finch)	17.4	47.9	6.E-02	2.E-01	5.E-02	9.E-02	2.E-02	8.E-02	2.E-02	3.E-02	1.E-01	4.E-02
Willie wagtail	3.09	34.2	4.E-01	1	3.E-01	5.E-01	3.E-02	1.E-01	3.E-02	5.E-02	6.E-01	5.E-02
			Mean habitat concentrations (mg kg^{-1})									
			1.09	3.79	0.92	1.63	1.09	3.79	0.92	1.63	1.75	1.75

**excludes relevant habitats; unmarked hazard quotient: Non-hazardous; ^{a}: Probably non–hazardous; ^{b}: Possibly non-hazardous; ^{c}: Possibly hazardous; N. Wet.: Proposed environment without the wet lands; NRH: Not a relevant habitat; Prop.: Proposed land use environment; Resi: Residential habitat.*

The total number of times each habitat poses a specified degree of risk (non-hazardous, probably non-hazardous, possibly non-hazardous and possibly hazardous) in each land use environment has been graphed and is presented in Fig. 4. From the graph it is evident that the proposed land use environments increase the degree of risk posed.

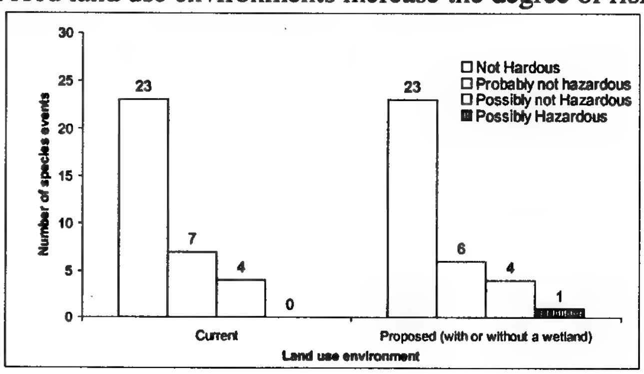

Fig. 4. The total number of times all habitats pose a specified degree of risk for current and proposed land use environments

DISCUSSION

By creating larger and more productive habitats at a site, birds may not have to search further afield for food, water and a suitable nesting environment. That is, the feeding and home ranges of birds may substantially decrease. As a result the proportion of food, soil and water ingested and air inhaled from the site will increase. If the site is contaminated, the level of exposure is increased through the increased ingestion of contaminated food, soil, and water and inhalation of air. Therefore in a more productive environment, the maximum level of soil

contamination that can be tolerated (PSC), must be lower to sustain the higher levels of exposure. The PSCs presented in Fig. 3 reflect this. For example, based on the feeding range of the grey currawong (CLW-ERA 2000), the woodland of the current land use environment may provide less than 20% of the grey currawong's source of food. However with the creation of more than 12ha of suitable habitat, the grey currawong may obtain up to 100% of its diet from the proposed environment. Principally as a result of this change in feeding range, the PSC dropped from >4.3 mg kg^{-1} to >0.8 mg kg^{-1}.

However for a number of birds, the creation of a wetland environment substantially influences the PSC, and opens up a major pathway of exposure, either through the ingestion of contaminated food or contaminated water. For the crimson rosella and rainbow lorikeet the main source of exposure is through the ingestion of contaminated water. For the red-browed fire-tail and willie wagtail the influencing source of exposure is through the ingestion of insects that have had an aquatic existence. For these birds the importance of the removal of the wetland from the proposal, substantially increases the PSC. However considering the level of contamination is substantially lower than the PSC for both scenarios, the level of risk is small and effectively remains unchanged (Table 2).

In addition to the parameters that influence the PSC, the level of contamination and the location of a habitat in relation to the contamination substantially influence the risk. For example, the mean level of contamination in the open grassland environment increases from 2.77 mg kg^{-1} to 3.79 mg kg^{-1} (Tables 1 and 2) as a result of proposing to extend this habitat over an area that was more highly contaminated. For birds such as the Australian magpie, which may rely substantially on this environment for food, the risk is shown to appreciably increase the HQ. However, the strategic positioning of proposed habitats can also have a dilution effect and may also substantially decrease the risk posed.

Figure 4 demonstrates that without considering the factors that influence the PSC and the factors that influence the level of contamination in each of the proposed habitats, the creation of new habitats can actually increase the overall risk.

Although the creation of new habitats at the Blackwood site increases the risk to terrestrial birds to a small extent with the contamination being possibly hazardous to only one species (Australian magpie-lark) in one habitat (open grass land), it illustrates the need to consider all the factors that influence risk before restoration begins. It should be noted however, that ecological risk rarely if ever, only involves one class of animal. As was the case with the Blackwood site, it generally involves a multitude of plant, invertebrate, and animal species that may be aquatic or terrestrial. The risks to invertebrates and plants was assessed according to Walker *et al.* (1997c), however the results are not reported here.

While a management program to manage the risk at the Blackwood site is relatively simple, involving simple remediation and modification to the proposal, the creation of some new productive habitats clearly has the potential to cause ecological damage.

CONCLUSIONS

It is evident that the types of habitat of an environment can greatly influence the risk a soil contaminant may pose. However, the degree of risk is also dependent upon the type of species and where the habitat is in relation to the contamination. Therefore in designing an ecological restoration program for a contaminated area, it can be of paramount importance to consider the types of species that will be attracted and the exposure pathways that may be opened as a result of the restoration. Otherwise, an ecological restoration could potentially create an ecological disaster.

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Synopsis and Future Direction from the TPH Criteria Working Group: Insight into Complex Mixtures

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ABSTRACT: The Total Petroleum Hydrocarbon Criteria Working Group has completed a five-year effort and published its fifth and final volume describing their approach developed to protect human health at petroleum release sites. This approach defined all petroleum mixtures as thirteen fractions according to expected transport properties of individual compounds. Most previous efforts to define toxicity criteria for human health risk assessment of complex petroleum mixtures used health effects information for only a subset of the chemicals in such mixtures. The Working Group developed toxicity criteria for each fraction using all available data, with emphasis on mixture toxicity information. With these data, the Working Group developed reasonably conservative reference concentrations (RfCs) and reference doses (RfDs) that account for uncertainty in the underlying toxicity database. The methodologies used by the working group to develop these criteria relied on categorically defined uncertainty assumptions that continue to be refined. As fraction-based approaches for petroleum risk assessment grow in use by states in the US and other countries, data gaps identified by the working group continue to be addressed. These include field demonstrations of the method and a recently completed fraction specific toxicity evaluation of the $EC_{>8}$-EC_{16} aromatic fraction.

KEYWORDS: jet fuel, Jet-A1, aromatic fraction, TPH Criteria Working Group, reference dose

INTRODUCTION

Petroleum release sites are difficult to evaluate because the composition and distribution of complex petroleum products often change following release to the environment. Total petroleum hydrocarbon (TPH) standards have often been applied to these sites which are remediated with an unknown reduction of human health risk. Recognising this dilemma, the Total Petroleum Hydrocarbon Criteria Working Group (TPHCWG) developed a fraction-based approach to risk assessment at petroleum release sites. The results of this work have been published in five volumes that outline the scientific basis behind the approach and provide the data used by the group in making its decisions (Vol.1 – Weisman 1998, Vol. 2 - Potter *et al.* 1998, Vol. 3 - Gustafson *et al.* 1997, Vol. 4 - Edwards *et al.* 1997 and Vol. 5 - Vorhees *et al.* 2000). The fraction approach is the basis for both the analytical method as well as the defined toxicity criteria and differentiates the working group approach from petroleum risk assessment or analytical methods that are defined solely by either a single indicator compound or by the whole product (gasoline or diesel). The Working Group's approach is a hybrid that employs both fractions and carcinogenic indicator compounds (benzene, and PAHs) in the overall risk assessment. The 13 fractions are designed to assess potential non-cancer effects and are grouped according to expected environmental behaviour.

These fractions are identified by equivalent carbon (EC) numbers, which are related to the boiling point of the compound and correlated to the retention time in a boiling point gas chromatography column normalized to the *n*-alkane compounds. The Working Group chose EC values since they more closely relate to environmental movement and because they provided the means for developing a GC-based analytical approach. The process in the development of the fractions used of the leaching to groundwater and volatilising to air models from ASTM RBCA. Leaching and volatilisation factors were plotted against equivalent carbon numbers for over 250 individual petroleum compounds and plotted against equivalent carbon numbers. Volume 3 (Gustafson *et al.* 1997) provides examples of various plots including the leaching and volatilisation factors. These initial plots demonstrated that aliphatics and aromatics behaved differently in the environment (aromatics are more water-soluble and slightly less volatile than aliphatics with similar equivalent carbon numbers) which was the basis of the major groupings for the Working Group fractions. These plots also demonstrated that within these groups the leaching and volatilisation spanned many orders of magnitude. The working group agreed that order of magnitude differences were significant and consistent with other uncertainties in toxicity and risk assessment and it was this difference that served as the basis for the 13 aromatic and aliphatic fractions. This distinction, on how petroleum products are grouped, allows investigators to model movement in environmental media and also allows the fractions to be treated as individual compounds, greatly simplifying both the toxicity assessment and overall risk assessment. Inherent in the fraction approach are the assumptions that are part of the ASTM RBCA models as well as the assumption that fraction properties do not change appreciably from product to product (i.e. the $EC_{>10}$-EC_{12} fraction in gasoline is the same as in diesel in terms of composition of individual chemical constituents) or with time following release to the environment.

Fraction specific toxicity criteria were developed with the goal of selecting a single value describing the toxicity of the entire fraction. Toxicity information was gathered from studies for whole products, petroleum mixtures, and individual petroleum compounds. The detailed search included published and unpublished toxicity studies for all components in these fractions (Edwards *et al.* 1997). The literature search revealed only 95 components with toxicity data, despite the fact that petroleum products contain thousands of compounds. Of the 95 components, only 25 had sufficient toxicity information to develop reference doses. Based on this review, the Working Group developed non-cancer toxicity criteria for each fraction based on individual component data or mixture toxicity criteria. The criteria were calculated using an approach similar to the US EPA methodology, which resulted in the development of reasonably conservative reference concentrations (RfCs) and reference doses (RfDs). These criteria ensure protection of human health and account for uncertainties in the underlying toxicity database (Edwards *et al.* 1997). These criteria are estimates (with uncertainty spanning perhaps an order of magnitude) of daily exposure to human population, including sensitive subgroups, that are likely to be without appreciable risk of deleterious effects during a lifetime. Some fractions share the same RfDs because their toxicity is believed to be similar.

Since there was limited petroleum toxicity data across the fractions, a smaller number of wider range fractions were developed to use when assessing potential human health risks. However, the total complement of the 13 fractions should still be quantified to obtain the necessary information about environmental behaviour.

As with the fractions, there are basic assumptions required when using the toxicity criteria.

(a) Fraction toxicity will not vary significantly from the compound or mixture used to develop the toxicity criterion for the fraction. These criteria are designed to account

for uncertainty in the toxicity database by overestimating rather than underestimating fraction toxicity.

(b) Application of each toxicity criterion is appropriate whether or not the compound or mixture from which the criterion was derived is present in the environmental samples (when possible, the Working Group relied on toxicity data from mixtures across the fraction).

(c) The toxicity of a given fraction does not change with different petroleum product sources (e.g. the toxicity of the $EC_{>10}$-EC_{12} aliphatic fraction is the same in gasoline and #2 diesel).

Volume 5 (Vorhees *et al.* 2000) provides summary information on the toxicity criteria for each fraction and critical effects noted in the key studies for compounds in each fraction.

The Working Group developed their fraction approach with assigned toxicity criteria for use within a tiered, risk-based decision framework to calculate risk-based cleanup goals for environmental media. The ASTM Risk Based Corrective Action provides the necessary framework and has been used in Working Group volumes to illustrate the approach. The approach is flexible and can be adapted and simplified to satisfy the needs of regulatory authorities or it can also be used as the basis for ecological assessment.

Fraction Specific Toxicity Study

The TPHCWG developed a proposed RfD of 0.04 mg kg day^{-1} for the $EC_{>8}$-EC_{16} aromatic fraction, using chiefly data on naphthalene. The Working Group concluded that RfDs assigned to the aromatic $EC_{>8}$-EC_{16} and $EC_{>16}$-EC_{34} fractions were more uncertain than those assigned to other fractions given the limited available toxicity data. Similarly, the Agency for Toxic Substances and Disease Registry indicated in their *Toxicological Profile for Total Petroleum Hydrocarbons (TPH)* that the "database for the aromatic fraction $EC_{>8}$-EC_{16} lacks information on a mixture or mixtures that could represent the entire combined fraction [...] Health effects data from these mixtures and from potential representative chemicals, including naphthalene, suggest some commonality of effect among constituents of the fraction" (ATSDR 1999).

A 90-day oral gavage study was conducted to assess toxicity of the $EC_{>8}$-EC_{16} aromatic fraction (Smith *et al.* 1999). This involved isolation of a large quantity of test material and a 90-day study. The $EC_{>8}$-EC_{16} aromatic fraction (boiling range 151-287°C) was prepared from Jet-A1 jet fuel, CAS no. 8008-20-6 (by Hazardous Substance Data Bank, 1991) by BDM Petroleum Technologies, Bartlesville, OK using a large scale silica liquid chromatographic column. The Jet-A1 jet fuel blended from different geographical locations was formulated and maintained by the U.S. Air Force Research Laboratory, Propulsion Directorate, Fuels Branch, Wright Patterson AFB, OH. JP-8 is the single fuel identified for use by all U.S. Department of Defense aircraft and vehicles and is typically referred to as the operational battle fuel for U.S. and NATO (North Atlantic Treaty Organization) allies (also known as NATO F-34).

Summary of $EC_{>8}$-EC_{16} Aromatic Fraction Subchronic Toxicity Study

The study was conducted to evaluate potential toxic effects of the $EC_{>8}$-EC_{16} aromatic test material in female Sprague-Dawley CD Rats and male C57BL/6 mice during and following daily oral administration over 90 days. The complete details of this study are presented in Smith *et al.* (1999).

Four groups of 15/rats/group and 15/mice/group were administered daily oral gavage dose of the test substance at 0, 20, 100, and 500 mg kg^{-1} in corn oil. Gavage volumes were the same for each species across dose groups. Clinical observations were conducted 1-2 hours after dosing and then again at 6 hours. Clinical pathology evaluations for hematology, coagulation and serum chemistry were conducted at necropsy. Following the 90-day dosing, all surviving animals were subject to necropsy with organ weight measurement and tissue collection for pathologic examination.

Clinical observations included lethargy in high dose groups of both species and low and mid dose groups of mice. Irritation from the test substance also caused short-lived (10-20 minutes after dosing) shovelling behaviour (where the animals pushed bedding material with its nose) and excessive salivation after dosing. There was an increase in food consumption in the high dose rat group and a sporadic decrease in the high dose mice. However, there were no significant differences in body weight for either species. Liver weights were significantly increased in the high dose rats, with observable increase in size (13 of 14 surviving animals) upon gross observation but there were no microscopic lesions identified which brings into question the toxicological significance of increased liver weights. The high dose mice also showed an increase in liver weight but this was not statistically significant. The livers were not enlarged in the mice and there were no microscopic lesions identified. Blood changes were recorded for mid and high dose rats with decreases in hemoglobin, hematocrit, and red blood cell counts. There were no microscopic lesions identified in either species across dose ranges. The critical effect of liver weight change was confirmed through an independent peer review by a board certified veterinary pathologist. From these findings it was concluded that daily administration of 20 mg kg day^{-1} of the Jet-A1 aromatic fraction was well tolerated in both species and that this dose represented the NOAEL for the test substance.

On-Going Work to Develop a Provisional Reference Dose

Based on the findings of this study, an effort is underway to develop a provisional reference dose for the $EC_{>8}$-EC_{16} aromatic fraction. In addition to using an approach similar to that found in Volume 4 (Edwards *et al.* 1997) to allow for a comparison to the work done by the Working Group, other methods, including data derived uncertainty factors and benchmark dose, will be utilised and compared. Appropriateness of uncertainty factors will be evaluated in light of the current literature and finally, recommendations for a fraction specific RfD will be made. Relevant toxicity information published after Volume 4 in 1997 will also be included in the review. This effort will provide a significant test to the practicality of the Working Group's approach as well strengthen some of the underlying assumptions.

CONCLUSIONS AND ADDITIONAL WORK NEEDED

This study fills an important data gap in our understanding of petroleum toxicity. However, additional research is warranted to further reduce uncertainty associated with the RfD for this fraction and other fractions with few data to support toxicity values. This work should include a two generation study with the $EC_{>8}$-EC_{16} aromatic fraction, and a study similar to that presented in this paper with the $EC_{>16}$-EC_{35} aromatic fraction.

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Sensory and Aesthetic Studies of Diesel Impregnated Soil

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ABSTRACT: Sensory studies were used to determine at what concentration diesel could be detected in soil. Using a range of diesel concentrations, a three-alternative forced choice method was applied to determine detection thresholds. The resulting mean detection thresholds were 2850 ppm for the clay/sand sample and 1850 ppm for the sand (for a 2 month old sample). The length of time diesel had been present in the soil appeared to have an effect on the detection threshold. After initial contamination, the detection threshold was at a low concentration, increasing until two months after contamination and then reaching a plateau. Visual descriptions of 'clean' and diesel-contaminated soil were also obtained, as were ratings of pleasantness of smell. The results indicated that diesel-contaminated soil can often be described more positively than uncontaminated soil. In some cases, soil with higher concentrations of diesel were rated as smelling more pleasantly than those with lower concentrations of diesel.

KEYWORDS: sensory, aesthetics, diesel, contamination, detection threshold

INTRODUCTION

Diesel contamination of soil is viewed negatively, often due to the perception of unpleasant odours wafting out of the ground, and other displeasing aesthetic qualities. The following study used sensory testing to determine at what concentration diesel could be detected in soil, whether diesel contamination influences a person's perception of the soils aesthetic values and how pleasant or unpleasant soil contaminated with diesel smells. The levels of diesel used in this study are below those that represent a health risk.

The study was conducted in two parts – Part 1 involved establishing a range of diesel concentrations to use for determining the level at which people can detect diesel in soil and whether soil type and temperature influence this range. Aesthetic visual ratings and pleasantness of smell tests were also undertaken. Part 2 was used to establish a mean level at which a sample of people could detect diesel in soil.

As there were a number of variables to be tested, the study was undertaken in two parts. Using this design our participants were not overloaded, or habituated to odour perceptions.

PART 1 INTRODUCTION

As mentioned, there were a number of objectives to Part 1 of the study. The main being to identify a range of diesel concentrations (parts-per-million (ppm) in soil) to be used for determining detection thresholds for a sample of people and whether soil type or temperature have an influence on thresholds. Other objectives were to obtain visual descriptions and pleasantness of smell ratings of soil contaminated by various concentrations of diesel as well as uncontaminated soil, and to determine whether soil type and concentration level influenced the results.

METHODS

Participants

A group of 16 individuals took part in the experiment. They ranged in age between 20 and 50 years old. Each participant undertook the University of Pennsylvania Smell Identification Test (UPSIT), a method used to quantitatively assess smell function. The group was categorised by gender, age and UPSIT diagnosis for further analyses.

Materials

Brown jars filled with soil and covered with sterile gauze were used for the odour section of the experiment. The dark colour of the jars and gauze enabled the participant to smell the sample without interference from their visual senses. When the samples were not in use, they were covered with lids.

Incubators were used to bring the samples to the correct temperatures (25°C and 15°C respectively) to represent typical summer and winter conditions (to test for influence of temperature on the range).

For the visual section of the experiment the samples were placed in medium sized petrie dishes with lids so as to decrease the influence of any odour from the soil on the participants' visual description.

Soil

Two types of soil were used – Soil Type 1 was Clay/sand (a loam) and Soil Type 2 a Sand. These were 'clean' samples (ie. not from an old petrol site). Fresh diesel was added to the soil to make up the initial chosen concentrations (0, 185, 375, 750, 1500, 3000, 6000, 12000, 20000 ppm). The diesel had been added to the soil just prior to the commencement of Part 1 thus this soil represented a recently contaminated site.

Procedure

Determination of a range of 'detection thresholds'

A three-alternative forced choice method with a modified 'Method of Limits' procedure was used. The forced choice method involves giving the participant three samples, two being controls (ie. uncontaminated) and the third sample containing a concentration of diesel. The participant must choose one of the three samples to be different.

The Method of Limits involves presenting a participant with a sample and recording whether or not they can detect the contamination. Starting from the lowest concentration and increasing the concentration, the participant answers no they cannot detect the contaminated sample or yes they can. Once their answer changes from no to yes that concentration is recorded as their threshold. The next set of samples is given in a descending order so as to reduce habituation. We chose to give the participant the samples in ascending order only, as this was principally an exploratory experiment. The participant was required to detect any difference in smell between three samples presented simultaneously. This process was repeated three times for each soil type and temperature combination.

This simple method was used as we had a number of conditions to be varied and felt using the procedure followed in Part 2 for this section would have resulted in the participants potentially becoming fatigued.

Visual descriptions

Eight descriptions of soil were chosen for this section of the experiment. A 4-point Likert scale was used for each of the descriptions. Participants were asked to rate each sample presented to them using the scales.

1	2	3	4
Dark			Light

Fig. 1. An example of a description scale used for the visual section of the experiment

Four samples from each soil type were chosen, the concentrations being 0, 6000, 12000 and 20000 ppm (diesel in soil) and presented to the participant in a random order. These concentrations were chosen as pilot studies indicated participants might become frustrated describing samples from all concentrations, as some were visually very similar.

Pleasantness of smell ratings

The participants were given eight samples (the same soil types and concentrations used in the visual section) in brown jars with gauze covering the opening. They were presented in random order and participants were asked to smell the sample and rate how pleasant they found the smell. A 5-point Likert scale was used ranging from pleasant to unpleasant or unpleasant to pleasant. The scales were alternated (in order) to control for anchoring effects.

RESULTS

Range of detection thresholds

Individual thresholds were determined as the mid-point concentration between the level at which they could not detect the diesel and the level at which they could (e.g. between 750 and 1500 ppm diesel in soil). This was calculated for each of the three replicates and the median of these three was used as the detection threshold for that individual. Statistics for the notional detection threshold are presented in Table 1.

Table 1. Mean notional detection thresholds (and ranges) for the four soil type and temperature combinations

Sample combinations	Notional Detection Threshold (ppm)		
	Mean	Minimum	Maximum
Soil Type 1 – Clay/sand, at 15°C	204	94	558
Soil Type 1 – Clay/sand, at 25°C	131	94	278
Soil Type 2 – Sand, at 15°C	311	93	561
Soil Type 2 – Sand, at 25°C	210	93	560

The results for all three sections of the experiment were not normally distributed, thus non-parametric statistical tests were used for the analyses.

A Wilcoxon Signed Ranks Test was used to determine whether there was a significant difference in detection threshold between the two soil types chosen and two temperatures used. The results indicated there was no significant difference ($p>0.05$) between the detection threshold of the sand/clay and sand. Nor was there a significant difference ($p>0.05$) in detection threshold when the temperature was raised to 25°C from 15°C.

Visual descriptions

Results gathered from the visual section of the experiment were analysed according to difference in soil type and difference in diesel concentration. When looking at soil type there were significant differences ($p<0.05$) overall between the way Soil Type 1 and Soil Type 2 were described (Table 2). An exception was for samples containing 12000 ppm diesel. There was no significant difference in the participants' description of Soil Types 1 and 2 at this concentration level.

Table 2. A comparison of the mean descriptions of Soil Types 1 and 2

Description	Soil Type 1 – Clay/sand	Soil Type 2 – Sand
Dark to light	Lighter	Darker
Healthy to polluted	Polluted	Healthier
Coarse to fine	Coarser	Finer
Starved to well nourished	Starved	Well nourished
Dry to moist	Drier	Moist
Attractive to unattractive	Unattractive	Attractive
Lumpy to even	Lumpy	Even
Not good for gardening to good for gardening	Not good for gardening	Good for gardening

Using the Friedman Test, we found there to be a significant difference ($p<0.05$) between the ranking of each concentration for all eight descriptions. There were two exceptions - when describing the coarseness and consistency of Soil Type 2 there was no significant difference between the four samples (i.e. concentrations).

Correlation testing was also undertaken to determine relationships between increasing diesel concentrations and visual descriptions. It was found that as concentration increased Soil Type 1 became darker in colour, finer in texture, appeared more nourished, moist, even and attractive and rated as better for gardening. For Soil Type 2 the colour became darker, appeared healthier, more nourished than starved, more moist and again better for gardening.

Pleasantness of smell ratings

Mean ratings of pleasantness of smell for the eight chosen samples are in Table 3.

Table 3. Pleasantness of smell ratings of samples (1=Pleasant and 5=Unpleasant)

Sample	Rating
Soil Type 1 – Clay/sand, 0 ppm diesel	2.87
Soil Type 1 – Clay/sand, 6000 ppm diesel	3.47
Soil Type 1 – Clay/sand, 12000 ppm diesel	3.80
Soil Type 1 – Clay/sand, 20000 ppm diesel	4.13
Soil Type 2 – Sand, 0ppm diesel	2.93
Soil Type 2 – Sand, 6000 ppm diesel	3.87
Soil Type 2 – sand, 12000 ppm diesel	3.27
Soil Type 2 – sand, 20000 ppm diesel	3.80

Generally, most samples were rated > 3 indicating participants found the smell unpleasant. The two samples with no diesel were < 3, though greater than 2.8, thus they could not be classed as pleasant.

A Wilcoxon Signed Ranks Test indicated there was no significant difference ($p>0.05$) in the way participants rated the two soil types at each concentration (e.g Soil Type 1 and 2 with 6000 ppm diesel have similar ratings of pleasantness of smell).

Friedman Test results indicated there were significant differences in pleasantness of smell ratings given to the four samples (different diesel concentrations) of Soil Type 1. For Soil Type 2 there were no significant differences in the pleasantness of smell ratings of the four samples.

There appeared to be a discernible positive relationship ($r=0.40$, $p<0.05$) between diesel concentration and pleasantness rating of Soil Type 1. That is, the higher the concentration of diesel in the soil the more unpleasant the participants found the odour. There did not appear to be a significant relationship ($r=0.18$, $p>0.05$) between diesel concentration and pleasantness of smell rating of Soil Type 2.

CONCLUSION

From these results we concluded that the range of concentrations originally chosen were sufficient for determining peoples detection thresholds in the next section of the study. These concentrations are 0, 187, 375, 750, 1500, 3000, 6000, 12000 and 20000 ppm diesel in soil.

When looking at aesthetic values it was found that where we would expect soil containing higher levels of diesel concentrations to be classed unfavourable in comparison to 'clean' soil, our participants (unknowingly) found the contaminated soil to be more attractive, healthier, well nourished and better for gardening. From this we can conclude that if no odour is coming from the soil it may not always be obvious the soil is contaminated (with diesel).

Pleasantness of smell ratings for the two soil types were interesting in that we found you cannot always assume people will find a higher concentration of diesel more unpleasant than a lower concentration, as illustrated by the results of Soil Type 2 pleasantness of smell ratings.

The conclusion drawn from Part 1 of the study is that diesel contamination of soil is not always associated with unfavourable aesthetic values and unpleasant smells.

PART 2 INTRODUCTION

Having established a range of diesel concentrations to be used in Part 1 of the study, Part 2 involved determining the concentration of diesel at which a range of people could detect it in soil ('detection threshold').

METHODS

Participants

Seventeen participants were involved in Part 2 of the study – fourteen of the original participants and three new participants. Again the group was categorised by gender, age and UPSIT score for further analysis.

Materials

New samples were made up in the brown jars as in Part 1. Again they were covered with lids when the samples were not in use. A thermometer was used to measure the temperature of the soil, as we did not use the incubators to bring the soil to a particular temperature.

Soil

The same two soil types were used for Part 2 as in Part 1 and the samples were taken from the same source as in Part 1. As the soil used in Part 1 was representative of a recently contaminated site (i.e. diesel had just been added to the soil), the soil used in Part 2 can be seen as representative of an older contaminated site. In this case, the source of the diesel had been removed and as the containers used were not gas proof, volatiles would have escaped resulting in the possibility that the odour may not be as strong, though the concentration of the diesel is essentially the same.

Procedure

This experiment consisted of two parts – determining a detection threshold for each of the two chosen soil types. Participants were given a break in between the procedure for the first soil type and second soil type. The first soil type used was chosen randomly for each participant.

The three-alternative forced choice method was used for this experiment (based on work undertaken by Laing *et al.* 1992). Starting from the lowest concentration we asked the participants to select the different sample of three (2 controls, 1 contaminated). If they could not identify the correct sample the concentration was doubled and presented to the participant. Once the participant could identify the contaminated sample a second set of three jars was presented at the same concentration. This was repeated if the participant again identified the contaminated sample. If it was identified correctly a third time this concentration was taken as the participants' detection threshold for the first replicate. This procedure was replicated three times for each soil type and the median value of the three replicates taken as the participants' detection threshold.

As we found no significant difference in the range of diesel concentrations due to the temperature variations used in Part 1 we chose to use one temperature for Part 2. We kept the samples at room temperature, which ranged from 24.5 to 26°C.

We chose to use both soil types as there was a difference in the way people rated the pleasantness of smell of the two soil types. Soil Type 1 was rated as increasingly unpleasant to smell as the concentration of diesel increased whereas for Soil Type 2 there was no correlation between concentration of diesel and pleasantness of smell.

RESULTS

The average detection threshold and range of values for our sample of participants are shown in Table 4.

Table 4. Mean (and range) detection thresholds for Soil Types 1 and 2

Soil Type	Detection Threshold (ppm) Mean	Median	Minimum	Maximum
Soil Type 1 – Clay/sand	2859.6	1494.8	747.8	11995.0
Soil Type 2 – Sand	1848.0	1495.4	747.4	5977.9

Nonparametric statistical tests were once again used for the analysis of results as the distributions of the results were not normal. A Wilcoxon Signed Ranks Test and a Friedman Test both indicate that while the above mean detection thresholds are different this difference was not significant ($p>0.05$).

Statistical tests were also conducted to determine whether or not there were significant differences due to gender, age and UPSIT 'diagnosis'. Using Mann-Whitney and Kruskal-Wallis tests we found there to be no significant difference in detection threshold due to gender, age and UPSIT diagnosis.

We tested for a correlation between age of participants and detection thresholds for the two soil types. Spearman's rho was calculated for the two soil types – Soil Type 1 = 0.16, $p>0.05$, Soil Type 2 = -0.07, $p>0.05$. These results indicate no significant correlation between the two variables for either soil type.

A final Wilcoxon Signed Ranks Test and Friedman Test were conducted to compare the detection threshold results (using the results of the 25°C samples) from Part 1 and Part 2. The results of these tests indicate there was a significant difference ($p<0.05$) in the detection thresholds obtained when the samples represented a recently contaminated site and an older contaminated site. One reason for this difference could be due to a methodological artefact because of changed procedures. To test for this, the results obtained from Part 2 were analysed simulating the methodology followed in Part 1. Statistical analysis of the results using these equivalent (Table 5) data resulted in significant differences ($p<0.05$) between the detection thresholds of the samples representative of a recently contaminated sample and 2 month old sample (the detection thresholds of the 2 month old sample was significantly higher).

Table 5. Wilcoxon Signed Ranks Test for significant differences due to age of soil sample

Wilcoxon Signed Ranks Test		Friedman Test	
	Soil Type 1 – Clay/sand		
Z	-3.20	Chi-Square	13.00
Asymp. Sig. (2-tailed)	0.00	Asymp. Sig.	0.00
	Soil Type 2 – Sand		
Z	-3.19	Chi-Square	13.00
Asymp. Sig. (2-tailed)	0.00	Asymp. Sig.	0.00

CONCLUSIONS

When looking at soil representative of a two-month-old diesel contaminated site, our sample of participants could on average detect the diesel at 2850 ppm for Soil Type 1 and 1850 ppm for Soil Type 2. There were a number of people who could detect the diesel at lower concentrations and others who could only detect it at higher concentrations.

We can also conclude that the detection thresholds are not dependent upon the participants gender, age or how they scored in the initial University of Pennsylvania Smell Identification Test.

Threshold detection appears to rise (i.e. higher diesel concentration) as the length of time the diesel has been in the soil increases. It is dependent upon the source of the diesel being removed (eg. tanks). This could be due to the lighter fractions of the diesel volatilising. In our case, the containers holding the samples were not gas proof thus the diesel vapour was able to escape. In this way our experiment mimics field conditions in decommissioned sites. As our time frame was only two months, the concentration of diesel in the samples is unlikely to have altered dramatically, though over much longer periods of time there may be a difference.

This study has resulted in the finding that although our participants could detect the diesel in soil at relatively low concentrations, when visually describing soils with higher concentrations they often viewed them positively and in some cases more positively than clean soil. This was also the case with some of the pleasantness of smell ratings, in some cases the higher concentration samples were rated more pleasant than the lower concentration samples.

FURTHER INVESTIGATIONS

The results of Parts 1 and 2 of this study indicate that threshold detection appears to rise as the sample containing diesel ages. A subsequent study looking at threshold detection for a soil sample contaminated 10 years ago with diesel was undertaken to determine whether this indeed was an ongoing trend. The same procedure as Part 2 was followed.

The resulting detection threshold for this sample was significantly ($p<0.05$) higher than that obtained for the recently contaminated sample. However, it was not significantly different to the detection threshold obtained for the 2 month old sample.

These findings indicate that following the initial 2 months after the source of diesel has been removed, the detection threshold of a diesel-contaminated sample will remain statistically constant. This may have implications for the time between removing the source of diesel from a site and redevelopment in cases where it is assumed that these areas are left 'fallow' for aesthetic reasons.

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Using Bioavailability as a Basis for Regulating Contaminants in Soil – Is it the Holy Grail?

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ABSTRACT: The concept of contaminant bioavailability has yet to make any impact on the regulatory framework for the soil environment in Australia, in contrast to the tiered assessment of contaminant bioavailability recently developed for the aquatic environment. For contaminants having significant background concentrations i.e. inorganic elements, the issue of bioavailability is a critical one in determining the extent of soil contamination and setting appropriate remediation targets. This is often acknowledged, for example in the recent National Environmental Protection Measure, but little tangible progress has been made in introducing and implementing the concept. Data linking element concentrations in soil to human and ecological effects are sparse for Australia and regulatory frameworks and guidelines to control contamination of soils rely heavily on data generated in countries of the northern hemisphere. The importance of bioavailability depends to a large extent on exposure pathways considered. The reliance on total concentrations of metals (many being trace element nutrients) is particularly problematic for environmental investigation levels (EILs), where exposure of plants and many soil organisms is dominated by the soil pore water pathway. Current EILs are therefore both overprotective and underprotective depending on soil characteristics which modify bioavailability. Bioavailability has been introduced into jurisdictions in Europe with regard to control of metal contamination of soils, and similar approaches could be used here in Australia. Various frameworks have been suggested, ranging from an algorithm approach using easily measured soil properties, selective extraction and measurement of a fraction of the contaminant, through to the development of mechanistic partitioning and organism response models. Regardless of the framework adopted, the concept cannot be regarded as a replacement for use of total contaminant concentrations, but as a refinement of the current system.

KEYWORDS: regulations, heavy metals, toxicity

INTRODUCTION

Anthropogenic activities are leading to increasing inputs to soils of both organic and inorganic contaminants. In order to prevent irreversible degradation of the soil resource and limit the exposure of organisms to unacceptable hazards, soil quality standards need to be set which enable regulators to recognise both the presence of soil contamination and the risk posed by the contaminant.

In terms of xenobiotic organic contaminants, determining the presence of contamination is generally straightforward: if the compound is present, then the soil is contaminated. For inorganic elements, determining the presence of contamination is more complicated, as soils naturally contain these elements in variable concentrations. If present, the greatest challenge is determining whether an organic or inorganic contaminant is hazardous. There are three systems currently in use for setting soil quality criteria for heavy metals in soils: 'totals', 'algorithm', and 'availability surrogate' approaches. This paper discusses the appropriateness

of these different systems for managing risk in the context of metal contamination in Australian soils.

Totals-based Systems

Totals-based approaches define acceptable soil quality criteria in terms of a maximum allowable total concentration (MAC) of metals in the soil. The most precautionary totals-based soil protection system, which has been adopted by some northern European countries including Sweden, (SEPA 1994) does not tolerate any increases in metal concentrations in soil and uses the total background concentration as the MAC. Any input of metals into the system must be matched by outputs from the system (e.g. removal in crops). This approach requires a good understanding of the background concentrations of metal in soils, certainly a better understanding than we currently have of the range of metal concentrations in Australian soils. Only very limited data indicate that background values and the National Environmental Protection Measure (NEPM) limit values overlap considerably at present (Table 1). Moreover, it requires comprehensive knowledge of metal inputs from various sources and potential outputs. However, compliance with such an approach ensures protection of even the most metal-sensitive species.

Table 1. Concentrations of metals found in Australian and New Zealand agricultural soils, primarily in horticultural regions (Barry 1997, CSIRO unpublished data), Australian Environmental Investigation Levels (EILs, NEPC 1999) and US EPA soil limits for sludge use on land

Metal	Background Range (Australia) ($mg\ kg^{-1}$)	Interim Urban EILs (Australia) ($mg\ kg^{-1}$)	MAC's for biosolid amended soils (USA)* ($mg\ kg^{-1}$)
As	1-20	20	20
Cd	0.02-2.0	3	20
Cr	2-700	400 (III), 1 (VI)	1500
Co	0.5-150	-	-
Cu	0.4-200	100	750
Pb	5-80	600	150
Hg	<0.01-0.15	1	8
Mo	0.2-5	-	10
Se	0.5-3.0	-	50
Ni	1-500	60	210
Zn	2-250	200	1400

* calculated from maximum cumulative pollutant loading limits without taking into account background concentrations of the elements in soils.

An alternative totals-based system is in use in the USA for regulating soil application of metal contaminated biosolids. Here, metal levels in soils are allowed to increase above background values to MACs defined by a risk pathway modelling process. The risk pathway approach that was used resulted in humans being calculated as the most sensitive endpoint for As, Cd, Pb, Hg and Se, and soil biota calculated as the most sensitive endpoint for Cr, Cu, Ni and Zn. However, it has been argued that a lack of data on metal toxicity to organisms and transfer coefficients for metals from soils to organisms resulted in underestimates of the risk of toxicity for the MACs that were eventually selected (McGrath *et al.* 1994). The maximum concentrations of metals allowed in agricultural soils treated with biosolids in the US is shown in Table 1.

The European Union (EU) also uses MACs to regulate contaminants in biosolid-amended soils. With the exception of Zn, there is no scientific basis underlying the concentrations that have been selected (Reiniger 1998). It is therefore somewhat concerning that Australia appears to have adopted these values as the basis for a variety of soil quality criteria regulations included in the National Water Quality Management Strategy (NWQMS) documents and NEPM EILs. The EU MAC for Zn in soil was lowered to 200 mg kg^{-1} following research which suggested that the economically important soil microorganism *Rhizobia* spp experienced Zn toxicity in at least some soils at the original MAC for Zn of 300 mg kg^{-1} (Chaudri *et al.* 1993).

There appears to be some confusion surrounding the issue of metal bioavailability. It is often inferred that as long as 100% metal bioavailability was assumed for determination of EILs and MACs, then the limit values will be highly conservative. This is true, but it should be remembered that the inherent assumption in the Australian EILs is that the bioavailability of *added* metals assumed to be 100%, not 100% of metals present in the soil. This is because the EIL values have been derived from a compilation of phytotoxicity studies using metals added as water-soluble inorganic salts. This ignores the importance of the soil in modifying contaminant bioavailability. Different components of soils can bind metals, temporarily or permanently removing them from the pool of metals which are accessible to organisms, hence reducing their bioavailability e.g. phosphorus binding Pb as chloropyromorphite ($Pb_5(PO_4)_3Cl$). Phytotoxicity is also the critical pathway used in the US EPA sludge re-use rules for setting soil MACs for Cu, Ni and Zn (Table 1). MAC values were derived from field studies with biosolids and hence are much less conservative than the Australian EIL values. There is considerable discussion of the level of protection offered by these values, as it is assumed the binding of metals by the added sludge persists in perpetuity.

The total concentration of contaminants in soils is easy to determine. However the use of this approach to assess and manage risk has the serious disadvantage of not considering contaminant bioavailability. This could lead to the contradiction that a MAC established for an 'average' soil may in fact be toxic to organisms inhabiting a sandy acidic soil where bioavailability is high, or be deficient for organisms (if the element is an essential nutrient) in a heavy textured high pH soil where bioavailability is very low. Clearly an alternative approach is desirable.

Algorithm Approach

In recognition of the problems associated with using totals-based approaches for regulating contaminants in soils, researchers have attempted to introduce modifying factors based on soil properties to enable a better approximation of metal bioavailability in different soil types. Soil properties that have been shown to be highly correlated to metal bioavailability include pH, clay and organic matter contents. Empirical models of the type created by Sauvé *et al.* (1998) have been demonstrated to be reasonably successful in predicting the most bioavailable form of metals, namely the concentration of metal in the soil solution, across a wide suite of soils using only total metal concentration, pH and in some cases organic matter content as the input parameters. Similar datasets are becoming available for Australian soils, and Fig. 1 shows a close relationship between Cd partitioning (between solid and solution phases) in a wide range of Australian soils, as a function of pH and organic matter content. Background concentrations of inorganic contaminants in soil in the Netherlands are modified using this type of approach (Lexmond and Edelman 1992), and ecotoxicity values are also normalised to a standard soil of 25% clay and 10% organic matter content. Empirical equations which depend on clay and organic matter content are then used to modify threshold

values for the specific soil of concern (van den Berg and Roels 1991), although the basis for the algorithms used is scientifically shaky. Furthermore, because these relationships do not describe the specific mechanisms involved in modifying metal bioavailability, they are usually subject to a wide degree of variability. Hence the widespread applicability of these relationships needs to be resolved before these models can be applied for regulatory purposes in Australia.

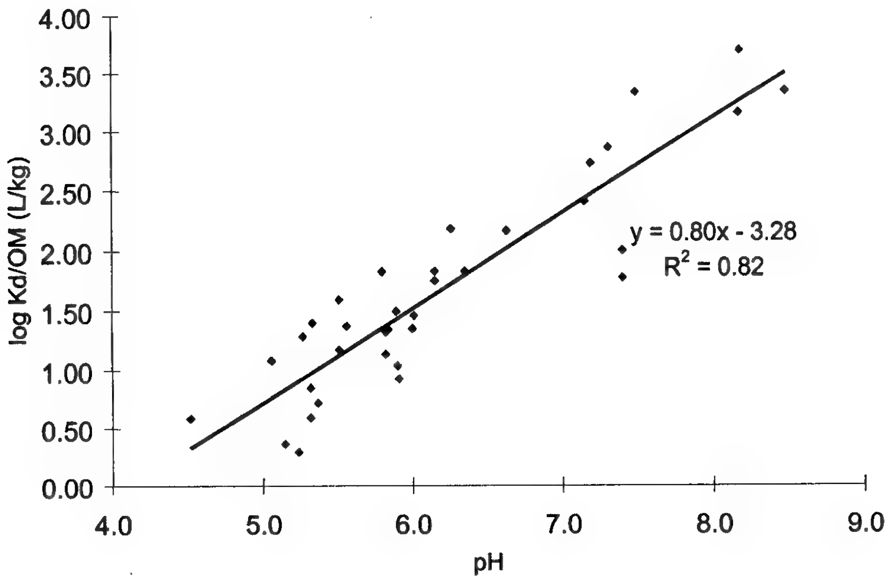

Fig. 1. Relationship between organic matter corrected Cd partitioning and soil pH across 35 diverse soil types in Australia (McLaughlin *et al.* unpublished data). Clay content varied from 1 to 59% across all soils.

Mechanistic approaches to assess bioavailability have become acceptable in risk assessments in the aquatic environment. The US EPA recently agreed to the use of the Biotic Ligand Model (BLM) to assess risks from metals in fresh and marine waters. This model describes the complexation reactions which reduce metal bioavailability in water, and also describes the interaction between metals and a biological membrane (fish gills). A similar model for terrestrial environments is lacking. One such attempt recently used best available knowledge of metal partitioning and complexation in soil, combined with ecologically relevant species toxicity threshold values, to assess risks from fugitive emissions of metals from smelters in the Canadian shield (Sheppard *et al.* 1999). Such an approach is perhaps the most scientifically-defensible, but the data needed to perform such an assessment for any Australian soil are still lacking.

Availability Surrogate

The best short-term measure of contaminant bioavailability in soils is a determination of the concentration of metals in target organisms actually growing in the soil of interest. This is impractical as a regulatory measure and countries such as Germany and Switzerland have turned to the use of neutral salt extractants as a surrogate for estimating heavy metal bioavailability. These extractants are used to extract the soluble and exchangeable pools of

metals in soils, pools which form the most bioavailable fraction of metals. The concentrations obtained are compared to an 'action value' which if exceeded, indicates a site in which contamination is potentially of concern. However, care must be taken in the use of neutral salt extractants for regulatory purposes, as there is no guarantee that they are capable of extracting all forms of bioavailable metals in all soils. Hence, there is the potential to underestimate the contaminant risk. Neutral salt extractants also only provide an indication of the immediate contaminant bioavailability, and therefore, the immediate risk. The residence time of metals in soils is on the order of thousands of years and so it is essential to have some understanding of the potential for long-term risks. For example, a neutral salt extraction of a soil with a high total concentration of heavy metals may register below the 'action value' if the soil is slightly alkaline (pH = 7.5). However, if in the long-term atmospheric pollution or soil management reduce pH, metal bioavailability may increase over time. It is therefore important to know which soils pose such potential risks in the long-term.

For human health risks, availability surrogates have been suggested for As and Pb, where an in vitro procedure to mimic the human gastric and intestinal system has been developed (Ruby *et al.* 1993, 1996). This is undergoing testing at present to allow adoption of the test by the US EPA as a surrogate for animal feeding bioavailability assessments.

Is Bioavailability the Holy Grail?

True assessment of soil metal bioavailability is technically feasible, however, techniques are presently used only in research studies e.g. animal feeding studies, human feeding studies using stable isotopic tracers or plant uptake studies using radioisotopic tracers. Such techniques could be used in a site-specific risk assessment, but the cost and time needed to perform these assay procedures means that, in all but the highest value sites, they are not used. From a risk assessor's viewpoint, bioavailability is indeed a holy grail.

In the site assessment and regulatory arenas, to obtain more realistic scientifically-based EIL and MAC values, surrogates for bioavailability assessment are therefore needed. We contend that use of total concentrations in soil alone is inappropriate. Adoption of either an algorithm based assessment or use of a bioavailability surrogate is needed to improve risk assessments of contaminated sites.

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Ecological Risk-based Cleanup Goals for the Protection of Terrestrial Receptors

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ABSTRACT: Ecological risk-based cleanup goals were developed for soils contaminated with a wide variety of organic and inorganic chemicals. The aim of the cleanup goals was to protect terrestrial receptors (i.e., plants, mouse, myna bird, and swamp harrier). Exposure to these receptors was characterised assuming the primary route of exposure to occur through ingestion of potentially contaminated food (prey organisms) and/or the uptake of soil from the site. Toxicity information was obtained from relevant literature. Cleanup criteria were calculated based on a hazard quotient (i.e., the ratio of exposure dose to toxicological benchmark dose) equal to one. The calculated cleanup criteria were then compared to typical background concentrations and to ecological investigation levels listed in the *National Environment Protection Measure for the Assessment of Site Contamination.* The results of this comparison indicate the potential for adverse effects to the terrestrial receptors at chemical concentrations below investigation levels. The results also highlight that without site-specific toxicity and bioavailability data, background concentrations may need to be used as cleanup criteria for many chemicals.

KEYWORDS: risk assessment, ecological, cleanup goals, background concentrations

INTRODUCTION

An industrial site impacted by a variety of chemicals including arsenic, cadmium, chromium, benzene, benzo(a)pyrene, chlordane, hexachlorobenzene, pentachlorophenol, and dioxins was to be redeveloped for residential landuse. The establishment of remedial goals included assessing target concentrations that would protect ecological receptors. Ecological cleanup goals, therefore, were developed for a range of potential terrestrial receptors selected as representatives of specific trophic levels. Because no site-specific toxicity or bioavailability data were available, conservative information from the literature was used in the development of ecological risk-based cleanup goals. Derived cleanup goals were then compared to ecological investigation levels and to published background concentrations.

RECEPTOR IDENTIFICATION

Exposure pathways for terrestrial receptors are primarily those related to exposure through consumption of contaminated plants or prey from the site. As part of the development of ecological risk-based cleanup goals for soils, ecological receptors were selected to represent key trophic levels within the terrestrial environment. These include a shrub (primary producer), the common myna, (common insectivorous bird), house mouse (*Mus musculus*) (insectivororous small mammal), and the swamp harrier (*Circus approximanus*) (a predator).

No protected species or sensitive habitats are currently located within the area. Ecological values associated with the site are expected to increase following remediation. Because of the proposed future use as a residential area, ecological values are largely

associated with the protection of native and introduced flora and fauna that may utilise the area in the future.

EXPOSURE ASSESSMENT

For all wildlife receptors, the primary route of exposure was assumed to occur through ingestion of potentially contaminated food (prey organisms) and soil from the site. The potential rate of exposure to chemicals of potential concern (COPC) was estimated through the modelling of COPC transfer through the food web and to the target receptor.

The potential daily intake of COPCs by each wildlife receptor (in milligrams per kilogram receptor body weight per day [mg kg^{-1} day^{-1}]) was estimated from the concentrations of COPC (maximum) in each of the ingested media (prey and soil) and the daily ingestion rate of each medium by the receptor. The potential rate of exposure to specific compounds was determined as the sum of the compound-specific ingestion rates from all media. A conservative modelling approach was taken to ensure that the estimated exposures are more likely to overestimate the actual potential exposure rather than to underestimate it. The following describes the methods that were utilised for the modelling of exposure for the wildlife receptors.

Exposure of the bird and mammals was modelled using the methods described in the USEPA's "Wildlife Exposure Factors Handbook" (USEPA 1993). The basic model for estimating the daily intake of a COPC per kilogram of body weight (through the ingestion pathway is as follows:

$$D_{Rx} = \frac{\sum_{k=1}^{N} C_{kx} \cdot F_k \cdot I_k}{BW_R} \tag{1}$$

where:

D_{Rx}	=	the estimated daily dose (mg kg^{-1} day^{-1}) of COPC x in wildlife receptor R
C_{kx}	=	the concentration of COPC x in the k^{th} food type, including soil as one of these types (mg kg^{-1} dry weight for food and soil/sediment)
F_k	=	the fraction of the k^{th} food type that comes from the contaminated site (assumed to be 1.0)
I_k	=	the ingestion rate of the k^{th} food type (kg dry weight day^{-1} for food and soil/sediment)
N	=	the number of food items in the wildlife diet (including soil/sediment)
BW_R	=	the body weight of wildlife R (kg wet weight)

With respect to incidental ingestion of soil, I_k was determined by multiplying the total food ingestion rate by the percent incidental soil ingestion. COPC concentrations in terrestrial biota were modelled from the environmental media concentrations used as the exposure point concentrations. The uptake models are based on transfer factors and are of the form:

$$C_O = TF_{M,O} \cdot C_M \tag{2}$$

where:

C_O is the analyte concentration in the target organism (in mg kg^{-1} dry weight)
C_M is the analyte concentration in an external medium (e.g. soil) (in mg kg^{-1})
TF_{MO} is the medium-to-organism transfer factor

For inorganics, the transfer factors for the earthworms, and small mammals were taken from literature sources with a default value of 1 for cases where no transfer factor could be found. The default value was not used for chemicals with biomagnification potential or that are known to bioconcentrate in earthworms (e.g., cadmium and zinc). The transfer factors for the organic COPC were principally derived from the logarithm (base 10) of the octanol/water partition coefficient.

For earthworms, the equation developed by Connell and Markwell (1990) was used to calculate the soil-to-earthworm transfer factor. This equation is:

$$TF_{S,W} = \frac{L_W \cdot K_{ow}^{b-a}}{x \cdot f_{oc}} \tag{3}$$

where:

$TF_{S,W}$ is the soil-to-earthworm transfer factor
L_W is the fractional lipid content in earthworms
K_{ow} is the octanol/water partition coefficient
(b-a) is a nonlinearity constant
x is a proportionality constant
f_{oc} is the fractional organic carbon content in the soil.

The values for the nonlinearity constant (0.05) and the proportionality constant (0.66) were from Connell and Markwell (1990) and were derived from earthworm studies. The lipid content of the invertebrates (0.84 percent of dry weight) was based on data for earthworms (Connell and Markwell 1990) and was used to conservatively estimate accumulation for a wider variety of invertebrates. The fraction of organic carbon in soil was assumed to be 2.8%.

For small mammals (the house mouse), a regression equation based on data presented in Garten and Trabalka (1983) was used to calculate the food-to-animal transfer factors. Because the transfer factors presented by Garten and Trabalka are based on uptake into fat, an additional term is included in the equation for the conversion from concentration in fat to whole body concentration. The resulting equation for deriving the transfer factors is:

$$\log(TF_{F,A}) = P_0 + P_1 \cdot \log(K_{ow}) + \log(L_A) \tag{4}$$

where:

$TF_{F,A}$ is the food-to-animal transfer factor
K_{ow} is the octanol/ water partition coefficient of the organic analyte
L_A is the fractional fat content in the animal
P_0 and P_1 are parameters derived in the regression analysis
log is the logarithm (base 10) of the term in parentheses.

For mammals, the values of P_0 and P_1 are –4.9409 and 0.8698, respectively (derived from rodent transfer factors presented in Garten and Trabalka [1983]). The fraction of body fat was assumed to be 10% for the estimation of whole-body COPC concentrations in house mice.

TOXICITY ASSESSMENT

Plant benchmark values that were used in this evaluation were primarily based on the information provided in Efroymson *et al.* (1997) and Sims and Overcash (1983). The former are based on lowest-observed-adverse-effect-levels (LOAEL). The endpoint of sublethal and reductions in plant growth may have no significant effects on the reproductive potential or the continued existence of a plant population. Furthermore, these benchmarks are primarily based on studies in which the chemical of interest is added freshly to a soil (in the case or inorganics, often as the most soluble salt) and is typically more bioavailable than the COPCs that have had a chance to bind with soil particles or are in a less soluble form.

Benchmark values that were used in the assessment of potential risks to wildlife receptors are based on information from the literature. Toxicity reference values (TRVs), as presented in EFA West (1998) were given priority in the selection of toxicity benchmarks for wildlife. The exception is the avian TRV for lead, for which the EFA West value was determined to be inappropriate for assessing potential risk to birds exposed to lead in soil and biota. Information from Sample *et al.* (1996) was used as second tier information. Emphasis was placed on no-observed-adverse-effects levels (NOAEL) for chronic oral exposure. NOAELs are defined as the maximum dosage tested that produced no effect that would be considered adverse to the long-term viability of the population. Therefore, the endpoints of particular interest in the underlying studies are those associated with reproductive health and development. In the absence of published benchmarks, such values were derived using the methodology described in Eqn (5) (Sample *et al.* 1996).

$$NOAEL_W = NOAEL_T\left(\frac{BW_T}{BW_W}\right)^s \tag{5}$$

where:

$NOAEL_W$ = the no-observed-adverse-effect-level for the wildlife receptor species ($mg\ kg^{-1} day^{-1}$)
$NOAEL_T$ = the no-observed-adverse-effect-level for the test species ($mg\ kg^{-1} day^{-1}$)
BW_T = the body weight of the test species (kg)
BW_W = the body weight of the wildlife receptor species (kg)
s = the class-specific scaling factor (s = 0.06 for mammals [Sample and Arenal 1999] and –0.15 for birds [Mineau *et al.* 1996])

Toxicity studies were considered to be chronic if they are conducted over a period of 26 weeks (one half year) or more. Studies of lesser duration (i.e. 1 to 25 weeks) were considered subchronic, unless they specifically included reproductive effects as endpoints (Sample *et al.* 1996). When only subchronic oral NOAEL values were available, they were converted to chronic NOAEL values by applying an uncertainty factor of 0.1 (Sample *et al.* 1996).

In cases when only a chronic LOAEL value was available for test data, an uncertainty factor of 0.1 is used to convert it to the chronic NOAEL. If only a subchronic LOAEL was available, then an uncertainty factor of 0.01 is used to estimate the chronic NOAEL. This uncertainty factor is the product of two uncertainty factors of 0.1, one to convert the subchronic value to a chronic value and the other to convert the LOAEL to an NOAEL.

When possible, NOAELs for the wildlife receptor species were derived from test species that are taxonomically close to the target receptor. For example, bird NOAELs were derived from avian test species and mammal NOAELs were derived from mammalian test species.

CLEANUP CRITERIA

Following exposure assessment and toxicity assessment outlined in previous sections, cleanup goals were derived associated with a hazard quotient (HQ) of 1.0. The HQ is defined by:

$$HQ = \frac{Exposure}{Benchmark} \tag{6}$$

where:

HQ = the hazard quotient (unitless)
Exposure = the estimated dose of the COPC for the receptor (in mg $kg^{-1}day^{-1}$)
Benchmark = the toxicological benchmark for the COPC and receptor (in mg $kg^{-1}day^{-1}$)

The HQ is greater than 1.0 when the estimated exposure to a COPC for a receptor exceeds the toxicological benchmark for that receptor. An Excel® spreadsheet was developed to calculate exposure, toxicity benchmarks, and HQs for each constituent and each receptor. Because the exposure model is linear, the HQ is a linear function of the soil concentration and the target soil concentration can be determined by setting the HQ equal to 1 (i.e., setting the exposure equal to the toxicity benchmark) and solving the resulting equation for soil concentration. By this means, the target concentration value was determined algebraically from the input parameters and was then checked by running it through the spreadsheet model to ensure that it resulted in an HQ equal to 1.

A two-phased approach was used to develop ecological risk-based cleanup goals for soil. Representative COPC were selected from the wide array of chemicals detected in soils to focus this examination of potential risk drivers within specific chemical groups. The initial phase involved a compilation of ecological investigation levels (EIL_{soil}) presented in the NEPC (1999) *Investigation Levels for Soil and Groundwater* for the representative COPC.

The second phase involved the development of cleanup goals (or modified EIL_{soil}) based on the methodology presented above with the use of a HQ of 1.0 to estimate ecologically protective soil concentrations for each receptor. Both EIL_{soil} and cleanup goals for plants, birds and small mammals are presented in Table 1. Background concentrations presented in NEPC (1999) are also presented in this table. Remediation levels should not be lower than background concentrations.

With respect to soil, ecological risk-based cleanup goals were derived for a shrub, common myna, house mouse, and swamp harrier exposed to representative COPC. The ecological risk-based cleanup goals are presented in Table 1.

Table 1. Ecological risk-based cleanup goals, investigation levels, and typical background concentrations

Chemical	Background Concentration (mg kg^{-1})[a]	NEPC EIL[b] (mg kg^{-1})	Plant Goal[c] (mg kg^{-1})	House Mouse Goal[d] (mg kg^{-1})	Myna Bird Goal[d] (mg kg^{-1})	Swamp Harrier Goal[d] (mg kg^{-1})
Inorganics						
Arsenic	1-50	**20**	10	0.39	251	
Cadmium	I	**3**	3	0.064	0.064	
Chromium	5-1,000	**400 (1)**[e]	1	4.0	11	
Copper	2-100	**100**	100	2.8	37	
Lead	2-200	**600**	50	13.8	0.05	0.02
Nickel	5-500	**60**	30	0.16	11	
Zinc	10-300	**200**	50	8.23	33	129
Organics						
Benzene	NA[f]	---[g]	---	**220**	---	---
Benzo(a)pyrene	NA	---	18	**7.0**	---	---
Chlordane	NA	---	---	24	**12.6**	40
o-cresol	NA	---	---	**2290**	---	---
p-cresol	NA	---	---	—	---	---
DDD	NA	---	---	4.7	**0.028**	0.06
DDE	NA	---	---	4.7	**0.028**	0.06
DDT	NA	---	---	4.7	**0.028**	0.06
Ethylbenzene	NA	—	---	**2,510**	---	---
Hexachlorobenzene	NA	---	---	8.21	**3.27**	24
Naphthalene	NA	---	**18**	418	---	---
Pentachlorophenol	NA	---	3	**1.67**	205	6,467
Phenol	NA	---	**70**	625	---	---
TCDD	NA	---	---	0.000006	0.00005	**0.00004**
Toluene	NA	---	**200**	202	---	---
Xylenes	NA	---	---	**15.5**	---	---

[a]Background concentrations reported in NEPC (1999).
[b]Values are Ecological Investigation Levels reported in NEPC (1999).
[c]Values derived as described under 'Toxicity Assessment'.
[d]Values in bold are the recommended ecological cleanup goals.
[e]Value in parentheses is for chromium III.
[f]Not available.
[g]No value available from NEPC (1999) or insufficient toxicity data for the derivation of a cleanup goal

DISCUSSION OF RESULTS

Due to the absence of site-specific toxicity and bioavailability data, the calculated cleanup goals are associated with a high degree of uncertainty and err on the side of conservatism. For this assessment, conservative assumptions were incorporated at many points in the process to provide assurance that these uncertainties will not lead to an

underestimation of the actual risk or to the development of cleanup criteria that are not ecologically protective. Specific examples of these assumptions include:

(a) wildlife receptors were assumed to feed exclusively within the confines of the contaminated site;
(b) trophic levels utilised in this assessment focused on species with food habits that are most likely to indicate the upper bound of bioaccumulation and biomagnification potential within the specific ecosystem under investigation (i.e. house mouse was assumed to consume only earthworms);
(c) NOAELs were used to address potential risk to wildlife receptors as opposed to LOAELs;
(d) laboratory toxicity studies used in the derivation of toxicity reference values for wildlife exposed to metals are largely based exposure of test species to the most bioavailable form of the chemical in question; and
(e) plant toxicity values were based on laboratory investigations where tests species were exposed to unweathered concentrations of chemicals applied directly to soil.

As is evident from Table 1, there is a potential for adverse effects to the terrestrial receptors at chemical concentrations below ecological investigation levels, which are based on plant toxicity. The results also highlight that without site-specific toxicity and bioavailability data, background concentrations may need to be used as cleanup criteria for many chemicals.

Higher cleanup criteria may be acceptable if exposure pathways are eliminated thereby removing the potential for risk. Clean fill may be placed above impacted soils to eliminate exposure pathways. No deep burrowing animals are expected to use the site in the future. The possibility does, however, exist for plant roots to come into contact with the COPC and for bioaccumulation and transport to occur. Further remedies to prevent exposure (e.g., use of a geotextile membrane to prevent root penetration, stabilisation of contaminants to prevent uptake by roots, or treatment of the waste to modify toxicity or bioavailability) will render such a strategy ecologically acceptable with respect to the terrestrial ecological receptors.

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Targets and Toolkits – The Development and Use of an Integrated Suite of Guidance and Protocols for Groundwater Protection in England and Wales

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ABSTRACT: Recent major changes to groundwater protection legislation in England and Wales are driving the production and implementation of new guidance and technical tools. Combined with an impending revision of its Groundwater Protection Policy, the Environment Agency has developed an integrated suite of policy, guidance and procedures to support its regulatory duties. The paper describes the regulatory framework and a selection of the supporting new tools, including tiered risk assessment methodologies, monitored natural attenuation guidance and associated software packages.

KEYWORDS: groundwater, legislation, risk assessment, remediation, natural attenuation.

INTRODUCTION

England and Wales have a legacy of groundwater contamination resulting from intensive industrial, agricultural and urban land use over the past 200 years, yet 35% of the potable water supply is obtained from groundwater (75% in southern England), with a substantial proportion of this being derived from inherently vulnerable aquifers.

Groundwater protection issues are currently receiving more attention arising from pressure to implement European Union (EU) directives and the need, as expressed in Government policy, to recycle brownfield land in preference to the development of greenfield sites. In the last two years there has been a sea change in groundwater protection legislation that is now driving the production of a substantial amount of new guidance and technical tools, with the prospect of further developments over the next ten years as the EU Water Framework Directive is implemented.

This paper describes some of the tools that have been developed by the National Groundwater & Contaminated Land Centre (NGWCLC) to meet the new legislative needs.

REGULATORY BACKGROUND

The Environment Agency (the Agency) is the principal regulator for groundwater protection in England and Wales, with a notable exception being contaminated land where it is the joint regulator with the Local Authorities. The NGWCLC acts as a centre of technical expertise within the Agency and also provides specialist support to Government departments, aiming to provide a degree of consistency on both technical and policy-driven groundwater protection issues. A key element in this role is the Agency's "Policy and Practice for the Protection of Groundwater" document (Env. Agency 1998), which contains policy statements and overviews of technical issues, legislation and good practice. This is currently undergoing a major revision, in response to the recent changes in legislation.

The two distinct origins of UK groundwater protection legislation are described below.

EU Legislation that is Directly or Indirectly Transposed into UK Law

This is focused on the prevention of pollution by the control of current activities via a system of permits for the discharge or disposal of polluting substances on or into land. Currently, the primary legislation is the Groundwater Directive (CEC 1980), which requires the protection of groundwater (the saturated zone) at the point of discharge.

Although the Groundwater Directive was published in 1980, for many years it was only partially transposed into UK legislation. In 1998, the implementation process was completed by the introduction of the Groundwater Regulations. These state that all List I (most polluting) substances should (with one or two minor exceptions) be prevented from entering groundwater completely. List II (less polluting) substances may be allowed to enter groundwater but must not result in pollution. All discharges or disposals of listed substances must be authorised and must be preceded by a "prior investigation" and their impact on groundwater checked, where necessary, by the "requisite surveillance" of groundwater.

The Groundwater Regulations also allow for the development of statutory Codes of Practice to protect groundwater from non-disposal activities (such as chemical storage) and give the Agency the ability to serve notices to prevent pollution where this is considered necessary. Other legislation passed in 1999 also enables the serving of Works Notices that require action (including remedial works) by operators should there be a likelihood of pollution or groundwater pollution has already taken place.

The combination of permits, notices and codes of practice, with strong enforcement powers, has now given the Agency a powerful suite of administrative tools for controlling groundwater pollution.

Driven by the Groundwater Directive, the above approach focuses on the assessment of, and reliance on, attenuation in the soil and unsaturated zones for List I substances, with an allowance for dilution at the water table for List II substances only. Groundwater itself is the receptor and is universally protected. The base legislation is fairly prescriptive and risk assessment can only play a limited role in the determination of consents etc., but this is a powerful driver for research and development into attenuation both in the soil zone and the underlying unsaturated zone, particularly with respect to List I substances.

UK-specific Legislation Relating to Historic Activities

In contrast, the legislation relating to soil and groundwater contamination arising from historic activities is UK-specific and more flexible. Also, groundwater beneath the site is not necessarily considered the prime receptor. This reflects the UK approach to the remediation of contaminated land only to a suitable-for-current-use basis, rather than to generic standards, applied nationally.

Part IIA of the Environmental Protection Act, 1990, which sets out the statutory procedures for formally identifying and remediating contaminated land, was implemented by the Contaminated Land Regulations in April 2000. These regulations and the substantial body of guidance that accompanies them, provide a new framework for dealing with historically contaminated land and groundwater. These procedures allow for the widespread application of both risk assessment and cost-benefit techniques. Attenuation and dilution can be taken account of both in the soil/unsaturated zones and the saturated zone, along the pathway to whatever has been determined to be the prime receptor(s). Whilst this is a pragmatic and cost-effective approach to the competing demands of soil/groundwater protection and re-use of contaminated land, the interface between the 'historic' and 'current activities' regimes can be problematic.

QUALITY STANDARDS AND FUTURE LEGISLATION

Agreement on the wording of the draft EU Water Framework Directive was reached in June 2000 and it is anticipated that this will be implemented over the next decade. Its effect will be dramatic, as the Directive requires an integrated approach to sustainable surface water and groundwater management and protection, including a strong emphasis on the characterisation and monitoring of groundwater and the reversal of adverse anthropogenic trends. For example, when a monitored adverse trend in groundwater quality reaches 75% of established EU standards, then action must be taken to reverse that trend.

In contrast to surface water and air, which have been subject to statutory quality objectives or standards for many years, currently there are no formal UK or EC groundwater quality standards. In the absence of these, statutory standards for drinking water (as supplied at the tap) and Environmental Quality Standards for surface waters (EQSs) tend to be used as reference points, but are often not appropriate to the hydrogeological situation in question. In the past, the UK has steered away from setting groundwater quality standards due to the difficulty of both characterising the range of natural groundwater quality across the very diverse hydrogeological environments present in the UK and applying any such standards in a consistent manner without imposing an undue burden on industrial or agricultural activity. The pressure to produce groundwater quality standards is now increasing due to both the existing and forthcoming EU legislation noted above.

TOOLS TO PRIORITISE CURRENT GROUNDWATER PROTECTION NEEDS

Over the recent years a series of tools have been developed to support the PPPG. Groundwater vulnerability maps at a 1:100 000 scale covering the whole of England and Wales have been produced, on which the land surface is divided into Major, Minor and Non-aquifers. The inherent vulnerability of the aquifers to pollution is indicated by subdivision of the land surface into areas of high, intermediate or low vulnerability, based on the type and thickness of soil and drift cover. Groundwater source protection zones (SPZs) have also been produced for around 2000 significant potable abstractions. For most sources, three zones are produced (Zone I – 50 day travel time, Zone II – 400 day travel time and Zone III – Total Catchment Zone). The Agency has recently completed the integration of the SPZ datasets on a GIS system and has made the maps publicly accessible on its website (www.environment-agency.gov.uk).

The vulnerability and SPZ maps may be regarded as risk screening tools that give an initial view of the inherent risk of groundwater pollution, should a pollutant source be present at the surface. Because of the scale and precision of the datasets they should not be used for detailed site-specific assessments. However, in combination with policy statements, they give a clear indication to developers, operators etc. of the likely risks to groundwater and the likely reaction of the Agency to prospective developments, particularly within a land use planning context. They also have a role in emergency planning, in prioritising pollution prevention activities and in identifying which parts of the source catchments may be the origin of potential or actual pollution.

RISK ASSESSMENT TOOLS - EXISTING DISCHARGES

A large number of new permits and reviews of existing permits are necessary under the Groundwater Regulations. The requirements for a prior investigation are potentially quite onerous, particularly as a large number of the disposals are relatively small scale and,

providing good practice is followed, there is little risk of groundwater pollution. Therefore, the Agency has produced a system of assessment that is appropriate to the scale of, and the risk presented by, the proposed discharge or disposal. This new framework for assessing disposals mirrors that developed for the contaminated land regime (see below) and a summary is given in Table 1. Initial risk screening tools have been developed and more detailed procedures for Level 2-4 assessments are in various stages of development and will be completed by 2001.

RISK ASSESSMENT TOOLS - CONTAMINATED LAND/GROUNDWATER

In 1999 the Agency produced its methodology for deriving remedial targets for contaminated soil and groundwater to protect water resources (Env. Agency 1999b). The methodology is a tiered, risk-based approach that draws heavily on approaches such as the RBCA procedure (ASTM 1995) but is applicable for all substances and takes account of not only the particular approach to contaminated land assessment in the UK but also existing water quality standards and other UK statutory requirements. Figure 1 gives a brief overview of the procedure. A series of spreadsheets that give deterministic solutions to the equations within the methodology are available on the Agency's website.

To support this approach, the Agency has promoted the development of the ConSim software package that uses the same analytical solutions to groundwater flow etc. as used in the remedial target methology (RTM), but coupled with probabilistic Monte Carlo simulations (Env. Agency 1999a). The output from ConSim is thus in the form of probabilistic plots. ConSim can be used in undertaking Tier 1-3 assessments under the RTM; the use of ConSim within this framework is described in Env. Agency (1998).

GUIDANCE ON MONITORED NATURAL ATTENUATION

Natural Attenuation (NA) is the *mechanism* whereby naturally occurring physical, chemical and biological processes act within an aquifer to reduce contaminant mass, concentration, flux or toxicity. Monitored Natural Attenuation (MNA) is a *remedial technique*, which is by definition a monitored activity. The acceptance of MNA, either in isolation or in combination with other treatments for remediating historically contaminated groundwater in the UK has increased in recent years, but it is not applicable to all hydrogeological circumstances and the approaches to demonstrate its effectiveness have varied widely. The Agency has developed technical guidance that not only provides a clear framework to assist with the design, evaluation and implementation of MNA strategies but also considers the specific hydrogeological conditions, most frequently found pollutants and prevailing legislative regime in England and Wales (Env. Agency 2000).

The lines-of-evidence approach set out in other NA protocols has been adopted and in verifying the performance of MNA, the main criteria for acceptance by the Agency are:

(a) confidence that it will be effective in protecting receptors throughout the monitoring period (and beyond) and that there will not be significant expansion of the plume of contamination into uncontaminated groundwater;
(b) the process can be adequately monitored to demonstrate predicted behaviour;
(c) remedial objectives will be achieved within a reasonable time frame (typically no more than one generation/~30 years), and will not be excessively long when compared with other remedial options.

The guidance document describes a four-stage assessment process:

(a) screening procedures to assess the viability of natural attenuation;

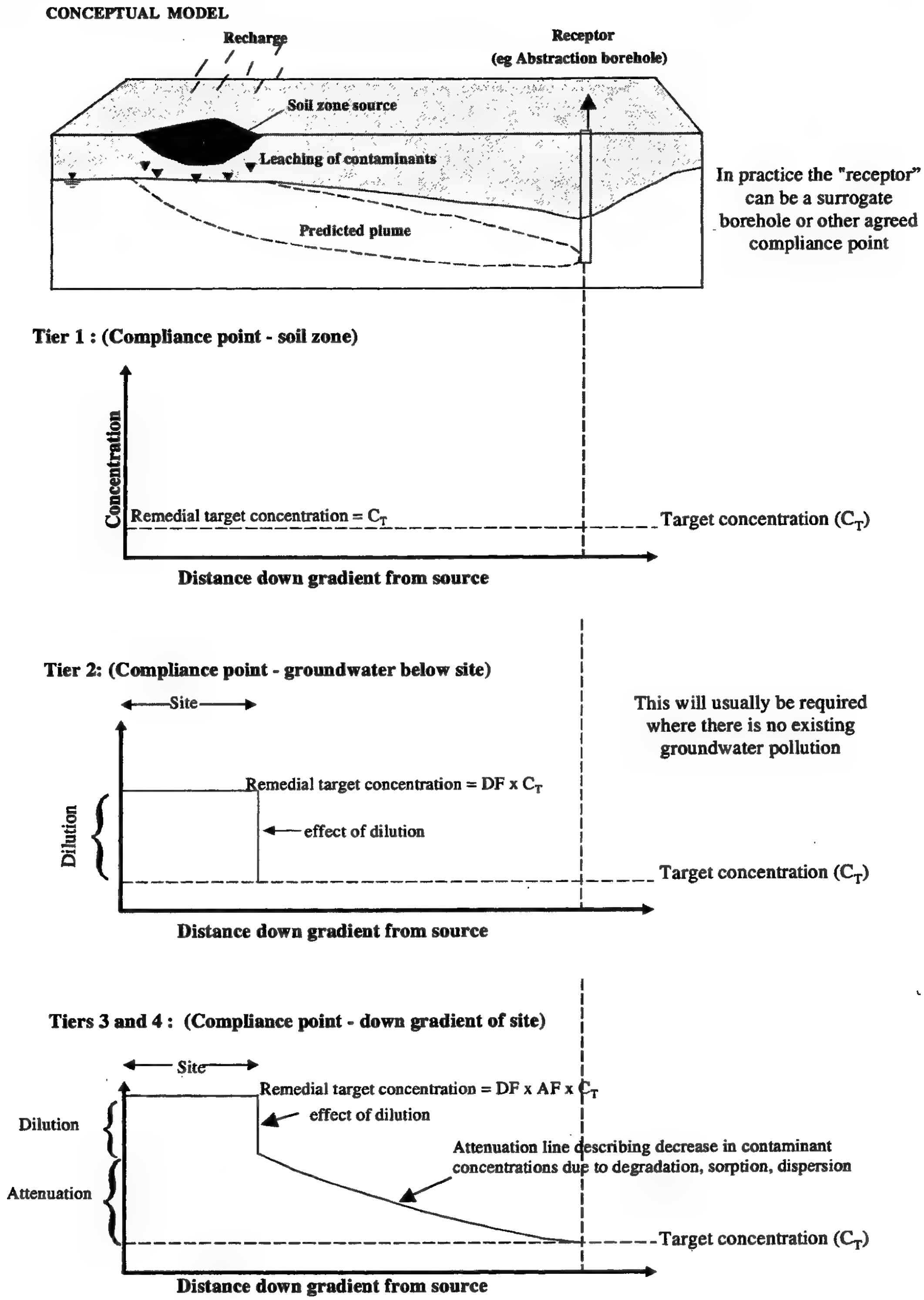

Fig. 1. Summary of remedial targets methodology (for soils)

Table 1 : Summary of technical assessment levels for current discharges and disposals under the Groundwater Directive

Level	Characterisation of	Substances of concern	Processes under investigation	Point of assessment	Data collection method	Assessment procedure	Parameters to be determined
1	Source material and inherent site sensitivity	List I and II	Overview of all processes	Not applicable	Desk study (primarily application form)	Initial screening assessment.	Hydraulic load, chemical load, soil type, unsaturated zone, aquifer, land use, topography, chemical properties, proximity
2	Source term and soil type/ characteristics	List I and II	Loading and attenuation in soil	Base of soil zone	Further desk study. Site inspection. Trial pits and shallow on-site boreholes. Substance analysis	Fate and behaviour assessment (soil). Site verification of application details. Assessment of samples. Calculations. Soil models.	Soil porosity (water and air filled), bulk density, fraction of organic carbon, pH, sorption characteristics. Soil type. Effective rainfall. Background concentrations of contaminants in soil. Contaminant properties, including solubility and density. Partition coefficient of contaminants: for organic contaminants, this can be calculated from the fraction of organic carbon and the organic carbon partition coefficient. Henry's Law constant. Degradation characteristics of contaminant in soil.
3	Unsaturated zone below soil	List I and II	Attenuation in unsaturated zone	Base of unsaturated zone	Trial pits and boreholes (site)	Fate and behaviour assessment (unsaturated zone). Assessment of samples. Calculations. Analytical equations. Models eg ConSim.	*Unsaturated zone :* Site-specific depth. Sorption characteristics. Physical characteristics (such as, fissure and intergranular hydraulic conductivity, bulk density, water and air-filled porosity) Degradation characteristics of contaminant in unsaturated zone.
4	Impact on groundwater	List II only, except where there are relaxations of the List I prohibition	Dilution at the water table	Water table beneath site	Boreholes (site and off-site)	Calculations. Analytical equations. Numerical flow models.	*Saturated zone :* Hydraulic conductivity, hydraulic gradient, saturated depth/mixing zone thickness, source dimension relative to groundwater flow. Background groundwater quality

Note : the Levels are normally progressive and incremental

(b) procedures to demonstrate current attenuation properties;
(c) procedures to evaluate longer-term attenuation capability; and
(d) procedures to verify attainment of the agreed remedial objectives.

LINKS BETWEEN PROCEDURES

A number of the procedures that comprise the groundwater protection toolkit in England and Wales are linked. For example, one of the screening criteria for applying MNA to contaminated land is the site's location with respect to SPZs. The data sources for the latter were developed primarily for assessing the risk from current activities on major groundwater sources. Similarly the tiered approach to assessment of the discharges and disposals under the Groundwater Directive was developed from the RTM procedures. Software tools such as ConSim can be applied across regimes.

However, there also can be dangers in such linkages and there is a need to ensure that any adapted procedures are fit-for-(new)purpose. In the example given above, if the decision on a candidate site for MNA rests heavily on its location vis-a-vis an SPZ, then the precision of and assumptions behind the definition of the SPZ must be recognised in this assessment.

The setting of quality standards for groundwater must also be undertaken with a view to all the regimes that potentially may be affected. Given the well-established basis for Drinking Water Standards (DWSs) (human health) and EQSs (based on toxicity to aquatic life), it is natural that these standards should remain as benchmarks for groundwater quality. However, such standards would be too restrictive if applied to the contaminated land regime and would effectively rule out MNA as a remedial technique. In addition, the natural variation in background quality must be factored in. The competing needs of the different regimes are best accommodated by considering the point of compliance rather than the development of different standards for different uses. Moving the point of compliance away from the pollutant source enables processes such as NA to be taken into account and can have a dramatic effect on the remedial targets in the source area (Fig. 2).

This pragmatic approach is now being applied in England and Wales but will have to be re-assessed within the context of the Water Framework Directive so that we can have a workable and reasonable approach to groundwater protection in the coming years.

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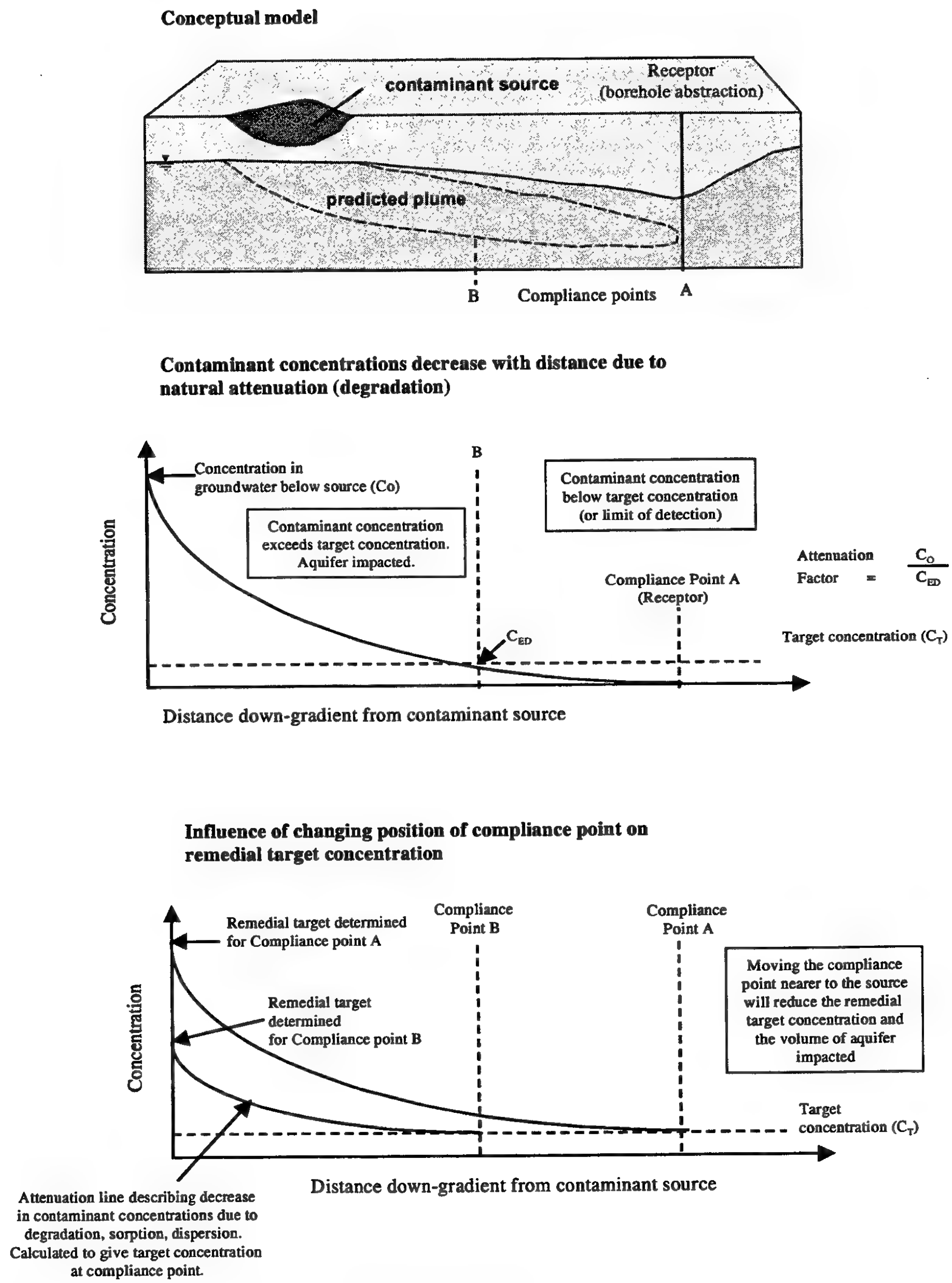

Fig. 2. Influence of natural attenuation on contaminant concentrations

An Integrated Process of Landfill Rehabilitation, How to Manage Contamination as Part of Numerous Other Issues

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ABSTRACT: The rehabilitation of former landfills for high-value development is increasingly required, especially close to urban area where demand is high. Such rehabilitation is a challenge as landfills have a number of issues (i.e. landfill gas, leachate, contamination, geotechnical, groundwater, planning approval, and community perception). This paper presents a case of an integrated approach to address some of the issues associated with a derelict landfill and achieve the objective of returning the land into a sustainable and high-value development outcome.

KEYWORDS: landfill, rehabilitation, integrated approach, groundwater, landfill gas, geotechnical

INTRODUCTION

The landfill site is located in the Suburbs of Melbourne. The site was excavated in the late 1960s for the supply of fill material for the low lying developing urban area. The site was then backfilled using inert waste (concrete and building rubble) and to a lesser extent industrial waste, such as plastics, grease etc. The landfill operated in a haphazard manner with little control on the type of dumped material and no compaction control.

The landfill site is located on the edge of a swamp approximately 1.5 km inland from Port Philip Bay and covers an area of 16000 m^2. The underlying sediments consist of Quaternary swamp deposits overlying Tertiary sediments. Groundwater is generally at a shallow depth and flows towards the Bay.

The site is capped with a layer of silty sand material between 0.5 and 1.0 m thick across the site. The underlying landfill material varies in thickness from 2 m up to 8 m. The underlying natural sediments of the landfill consisted of minor sand in silty swamp deposits.

METHODOLOGY

Our methodology for the rehabilitation of the site took into consideration all the issues associated with the site as a combined approach, which offered an economic solution to the investigation requirements. Issues that needed to be addressed included soil and groundwater contamination, landfill gas and geotechnical stability of the site.

A background study was carried out to identify potential contaminants as a result of previous land uses. The background study consisted of the following elements:

(a) determination of the physical, geological, hydrogeological and topographical setting of the site;
(b) review of Local Government records, any previous site assessments and historical records; and
(c) site inspection.

The background study enabled a more accurate focus of the soil, landfill gas, groundwater and geotechnical investigation program.

The field assessment of the soil, groundwater, landfill gas and geotechnical issues involved the following works:

(a) drilling at 15 points to depths of up to 12.0 m on a grid pattern across the site;
(b) the excavation of 10 pits to depths of up to 2.5 m using a backhoe;
(c) the installation of four groundwater bores, three into the landfill and one into the underlying natural material;
(d) the installation of four gas monitoring bores;
(e) the collection of 67 soil samples (including four blind, five split duplicate) from across the site;
(f) the collection of five groundwater samples (including one split duplicate); and
(g) the collection of four landfill gas samples.

RESULTS

Soil Investigation Results

The geology encountered during the excavation of sampling pits and boreholes, consisted of a capping layer ranging in thickness from 0.5-1.5 m (mostly sand, silty sand, sandy clay) overlying refuse fill. The natural sands, sandy clays and clayey sands were encountered at depths ranging between 6.2-8.7 m below ground level.

Contaminants found within the 'capping fill'

The pH of the soil ranged from 6.8 to 10 for the capping fill material. Copper was detected above the ANZECC B guideline (ANZECC/NHMRC 1992) value of 60 mg kg^{-1} in 9 locations within the capping fill across the site, ranging from 63 to 290 mg kg^{-1}. These locations were at the northern part of the site and the central part of the site. All of the elevated copper concentrations were below the NEHF-A residential HIL guidelines (1000 mg kg^{-1}) (Imray and Langley 1996).

Zinc was recorded at concentrations above the ANZECC B guidelines (200 mg kg^{-1}) in the capping fill around the central area of the site in 4 samples ranging from 430 to 1800 mg kg^{-1}. However, all elevated concentrations were below that of the NEHF-A residential HIL guidelines (7000 mg kg^{-1}).

Lead was recorded at concentrations above both the ANZECC B (300 mg kg^{-1}) and NEHF-A guidelines (300 mg kg^{-1}) in two locations at 1100 mg $kg^{-1}$and 2200 mg kg^{-1}.

Cadmium was detected above the ANZECC B Guidelines (3 mg kg^{-1}) within the capping layer at 3.5 mg kg^{-1}) however, well below the NEHF-A Guidelines (20 mg kg^{-1}).

All other contaminants analysed for were below laboratory detection limits or well below the assessment guidelines.

Contaminants found within the 'refuse fill'

The pH of the sediments within the refuse ranged from 6 to 8.8. Copper was found in nine locations above the ANZECC B criteria (60 mg kg^{-1}) across the site, within the refuse fill ranging from 85 to 960 mg kg^{-1}. However, all were below the NEHF-A guidelines (1000 mg kg^{-1}). These locations were within the northern and central parts of the site.

Zinc was detected at elevated concentrations above the ANZECC B criteria (200 mg kg^{-1}) in 12 locations across the site within the refuse fill ranging from 240 to 12000 mg kg^{-1}. Only one to exceeded the NEHF-A guidelines (7000 mg kg^{-1}) for zinc.

Lead was detected above both ANZECC B (300 mg kg^{-1}) and NEHF-A guidelines (300 mg kg^{-1}) in three locations within the refuse fill. One sample had a lead concentration of 6200 mg kg^{-1}over 20 times both the ANZECC B and NEHF-A guidelines. The other two locations where lead exceeded the guidelines were TP5 630 mg $kg^{-1}$and 1000 mg kg^{-1}.

Cadmium was found within the refuse fill in two samples above the guidelines (43 mg kg^{-1} and 5.6 mg kg^{-1}) ANZECC B criteria (3 mg kg^{-1}). One sample exceeded the NEHF-A (20 mg kg^{-1}) residential HIL guidelines.

Elevated nickel concentrations were found in the refuse fill at three locations (100 mg kg^{-1}, 94 mg kg^{-1} and 110 mg kg^{-1}) above the ANZECC B criteria (60 mg kg^{-1}), however, below the NEHF-A (600 mg kg^{-1}).

Tin exceeded the ANZECC B criteria (50 mg kg^{-1}) within the refuse at one location (140 mg kg^{-1}). Chromium also exceeded the ANZECC B criteria (50 mg kg^{-1}) within refuse at (76 mg kg^{-1}) and both the ANZECC and NEHF-A guidelines (100 mg kg^{-1}) at TP3 (660 mg kg^{-1}). TPH contamination was found in the refuse at three locations 3560 mg kg^{-1}, 6200 mg $kg^{-1}$and 1730 mg kg^{-1}) above the ANZECC criteria for TPH>C10 (1000 mg kg^{-1}).

Contaminants found within the 'natural material'

The pH of the natural sediments ranged from 7.7 to 8.0. A slight elevation of arsenic (21 mg kg^{-1}) was detected above the ANZECC B guidelines (20 mg kg^{-1}) within the natural material. No other contaminants of concern where detected above the guidelines in the natural material.

Groundwater Investigation

Refuse aquifer

Groundwater in the refuse was encountered at a depth of approximately 1.5 to 2.0 m below ground level. Four groundwater samples were collected from the three bores drilled into the refuse aquifer (including one duplicate). The concentrations of contaminants in the groundwater, within the refuse were above the ANZECC fresh water ecosystem guidelines (ANZECC 1992) for Cr (0.01 mg L^{-1}) and Zn (0.005 mg L^{-1}). However, only one sample recorded Zn (0.095 mg L^{-1}) above the ANZECC marine water ecosystem guidelines (ANZECC 1992) of 0.05 mg L^{-1}. TDS results ranged from 1600 to 2500 mg L^{-1}. Total nitrogen for all samples was elevated. Pesticides and VOCs were all below detection limits.

Natural aquifer

The sample of groundwater collected from the bore constructed into the natural aquifer beneath the site, contained concentrations of Ni (0.019 mg L^{-1}) and Zn (0.07 mg L^{-1}) above the ANZECC fresh water ecosystem guidelines (Ni - 0.015 mg L^{-1}, Zn - 0.005 mg L^{-1}) and marginally above the ANZECC marine guidelines (Ni - 0.015 mg L^{-1}, Zn - 0.05 mg L^{-1}). The TDS was 6500 mg L^{-1}.

Landfill Gas Investigation

The results from the landfill gas investigation show concentrations of methane above the lower explosive limits (LEL). Two of the landfill gas monitoring bores recorded gas within the explosive limits for methane, whilst the other two landfill gas monitoring bores had concentrations of methane above the Upper explosive limit. The landfill gas pressures were comparable to atmospheric pressure at the time of measurement.

Geotechnical

The results of fieldwork indicate that the subsurface conditions are extremely variable across the site. A capping layer typically consisting of loose to medium dense silty sand materials, varying in thickness from 0.5 to 1.0 m, covers the site. Underlying this is 6.0 to 7.0 m of loose refuse, thickness of which occasionally varies locally and reduces at the northern and southern parts of the site. The refuse encountered by the investigation boreholes was varied and included, paper, plastic, rubber, concrete, bricks, clay, wire and rope.

This is underlain by natural ground consisting of alternating layers of high plasticity greenish grey and brown, stiff to very stiff clays and sandy clays as well as grey and brown, medium density to very dense sands and silty sands. Refusal was encountered by SPT tests in a number of bores at a depth of approximately 12.0 m indicating hard strata.

Groundwater and seepage was observed in a number of boreholes during the investigation indicating that the groundwater table was generally 1.6 to 2.0 m below the ground surface.

DISCUSSION

Soil

Capping material

The sample results indicated heavy metal contamination from copper, lead and zinc within the capping layer of the site. Two samples within the capping layer, recorded concentrations for lead above NEHF-A guidelines. The heavy metal contamination is a likely result of the use of the site for storage of demolished construction materials including galvanised iron and plumbing fittings. The storage of galvanised iron across the site could have been the source of zinc contamination whilst the plumbing fittings could have contributed to the lead and copper contamination.

As part of the geotechnical works and preparation of the site for construction, the capping material is to be removed and recompacted and a clean clay cap of approximately 500 mm compacted over the current capping material.

Refuse

Based on the drilling programme, the majority of the waste consists of soil, concrete and hard waste.

The analytical results for the refuse fill indicate random contamination within the fill due to the uncontrolled use of the landfill in the 1960s-1970s. The refuse fill contained some high concentrations of heavy metals and TPHs across several hotspots.

The analytes list chosen to characterise the refuse material was extensive and covered a broad range of potential contaminants. Given the random distribution of waste and the possible variety of material dumped in the landfill, it was impossible to fully characterise the waste. However, the sampling and analytical programme implemented did give a general description of the waste.

The analysis of asbestos was not conducted, it is likely that asbestos material was dumped in the landfill, the distribution of asbestos within the waste would expect to be random.

Natural sediments

The elevated concentration of arsenic in the natural soil beneath the refuse material is likely to represent minor contamination deriving from the refuse material above. Not all sampling bores could be extended to the natural material due to refusal encountered. Based on the fine texture (ie. silty to silty loam) of the natural material and the analysis programme, it would appear that minimal contamination of the natural sediments has occurred as a result of the landfill.

Groundwater

Refuse aquifer

The type and concentration of contamination detected in the groundwater from the landfill are typical of a leachate from an old landfill. The low total dissolved solids (TDS) of the refuse groundwater are likely to result of surface water infiltration through the sandy capping material. The groundwater flow direction measured at the time was towards the west (towards the Bay); this was measured after a very dry period. However, groundwater flow direction is likely to vary seasonally.

Due to the sites location and the likely discharge of groundwater into the nearby estuary and bay, the marine water ecosystem criteria is the most appropriate - only Zn was detected above this criteria.

The natural aquifer adjacent to the refuse consists of silts and silty sands, which would tend to relatively restrict the mobility of contaminants from the landfill. Given the salinity of the local aquifer and the residential area, the beneficial use of the groundwater is for the protection of ecosystems.

Natural aquifer

The underlying aquifer does not appear to be impacted greatly by the groundwater within the refuse, with the exception of Ni and Zn contamination detected. The salinity of the natural aquifer is double of the refuse aquifer. This suggests that little mixing of the two aquifers is occurring.

Landfill Gas

The landfill gas analyses indicate that there is methane gas within the refuse material. The pressure measurements, were low, which would indicate that gas production from the refuse, is low. This would be expected from the chemistry of the methane production from a landfill that has been closed for over 20 years and has not been capped with low permeable material. The majority of the landfill gas production has already occurred and the gas escaped. Any on going minor gas production is currently free to escape and no build up is likely to occur.

Exposure Risk

In assessing the exposure risk of the site, the final development must be taken into consideration. The current capping material is to be stripped back and the underlying refuse material compacted with an impact compactor. The capping material will then be placed back and compacted. A 200 – 300 mm layer of large crushed rock or concrete lined with geofabric will be then placed on top to form a venting layer, which will be vented at the permitter of the site using passive vents. The building will be constructed on 'waffle'-type concrete slabs,

which sit on/above the compacted clay and have cavities. These cavities would be passively vented to prevent gas build up. A final layer of 300 mm of topsoil would be placed over the non-paved areas.

Over 800 mm of clean compacted material (venting layer, clay cap, topsoil) will be placed over the current sandy capping material, which based on our sampling/analytical programme contains minimal contamination. This 'clean' cap eliminates the risk of exposure to any soil contamination by residents of the property. The low levels of contamination detected do not pose a health risk to workers on the site during construction, however, a health and safety plan will address these issues.

The final proposed landscaping plan for the site is for shallow rooted plants that will not penetrate into the contaminated material, therefore eliminating the risk of plant uptake of soil contamination. Any vegetables grown on the site would be in "clean" topsoil.

The exposure to 'soil' contamination within the refuse is eliminated by the 800 mm of clean compacted material and approximately 500 mm of the former sandy cap. This layer eliminates exposure to any 'soil' contamination detected or undetected (including asbestos) in the refuse material.

The establishment of a venting layer across the entire site eliminates the risk of exposure and build up of landfill gases or other volatile compounds (gas will travel along the path of least resistance). It is possible that landfill gas production may be increased for a short period during recompaction of the waste, however, the venting layer will intercept any gas. In addition to the venting layer, the foundations of the building are on top of the compacted clay layer and any cavities are vented, this will also prevent any gas build up.

Currently surface water is free to infiltrate the sandy cap and mobilise contamination both in the capping material and the landfill. This current situation is likely resulting in mobilisation of contaminants from the landfill into the wider environment through the groundwater. However, based on the groundwater monitoring conducted to date, it would appear that the contamination is low and mobilisation of the majority of the contaminants may have already occurred and are undetectable due to dilution. This is evident through the low TDS recorded in the refuse groundwater, suggesting fresh water infiltration. Under the current situation, the risk of contamination mobilisation from the refuse to the wider environment, although low, must still be considered as a possibility. However, the proposed capping and development of the site (stormwater drainage) will reduce the surface water infiltration to the landfill dramatically. The elimination of surface water infiltration will greatly reduce the risk to the wider environment posed by the groundwater and result in the protection of the identified beneficial uses of the groundwater.

The exposure of residents of the property to groundwater is eliminated through the final cap design and the supply of town water. Based on TDS values, groundwater is not suitable for the domestic supply. The exposure of workers during construction to the groundwater will be minimal and will be addressed in a health and safety plan.

The main exposure pathway will be to workers during the earth works phase of the construction. However, given the low levels of contamination detected and the application of appropriate work procedures (such as dust control), exposure to contaminants by workers and nearby residents would be minimised or avoided. Based on the geotechnical findings, little or no excavation of refuse material would be conducted during the construction phase.

Exposure of the residents to the groundwater is not considered as a pathway, as groundwater will not be utilised on the site. Exposure by workers during construction will be minimal, as the majority of the works will be conducted above the water table.

CONCLUSIONS

Based on the finding of the investigation the following conclusions can be made.

(a) The contamination in the refuse material is variable and given the past uncontrolled dumping of waste, hot spots within the refuse would be expected.

(b) The natural deeper sediments do not appear to be impacted by past activities on the site.

(c) The groundwater within the refuse has being impacted by the refuse, however, is not considered a risk to users of the site.

(d) The deeper natural aquifer does not appear to be impacted by the upper refuse aquifer to any great extent.

(e) The geotechnical preparation of the site requires a compacted layer, which will be made of the existing capping material (0.5 m) and venting layer, imported clean fill and topsoil (0.8 m). This top layer will eliminate exposure of the residents to contamination within the cap and the refuse material.

(f) The construction of a venting layer and venting of raised concrete 'waffle' slabs will eliminate the risk of methane gas or volatile compounds building up within the buildings.

(g) The approach followed for the rehabilitation of this former landfill proved that an integral strategy, which takes into account and combined the different issues involved, is an effective process. Such a process has the ability to restoring a low value land into a high value resource and hence is on the heart of sustainable development and resource life management.

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Tracking Contamination Fate from Source to Impact: A Case of a Development Approval for the Rehabilitation of a Hydrocarbon Contaminated Site

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ABSTRACT: Contamination of a Queensland former service station site occurred via diesel leaking from underground storage tanks prior to the site being purchased for a shopping centre development. The objectives were to assess the contamination, any potential risk and any remediation so that a statutory development approval can be obtained together with an EPA-approved site management plan (SMP). This paper details the methodology and integrated approach used consisting of site history, problems of delay faced by the developer caused by inadequate contamination level investigation, human health risk assessment, development and satisfactory outcome of the SMP, and remediation stages. The lessons and the benefits learned in tracking contamination fate and extent, and the consequent risk assessment of the contamination impact in hydrocarbon-contaminated sites, are discussed. The value of justifying to the property owners the need to undertake adequate assessment at an early stage rather than taking a reactive approach, is also addressed with details of the repercussions.

KEYWORDS: diesel contamination, groundwater, remediation, risk assessment

INTRODUCTION

An old service station site in a central Queensland town, proposed for a shopping centre development was purchased with only a legal check as to the existence of the site on the Environmental Protection Agency's contaminated land register. On progressing with the development, diesel contamination was discovered. A more detailed contamination assessment found groundwater contamination necessitating the development and approval of a statutory site management plan (SMP) and a remediation plan. A number of assumptions were made causing additional problems with progressing the development. This paper details the work undertaken in assessing the extent of contamination, delineating the methodology required to ensure containment and possible remediation and developing a SMP to ensure appropriate management of the contamination during construction and operation of the shopping centre.

SITE HISTORY

In 1993 when the ownership of the service station changed, old fuel storage tanks (USTs) were replaced and a limited assessment of the contamination of the site was undertaken. No contamination was reported down to 4 m and no assessment carried out below this level. A search of the Contaminated Land Register under the old Queensland Contaminated Land Act found that no registration existed for the site. The purchase of the site proceeded, only to find that a clerical error had been made in the search and the site was not only on the register as a possible site, but the site was contaminated. In August 1999, the

USTs installed in 1993 were removed. While these tanks were intact, contamination was found to have occurred in the original tanks at levels below 4.5 m. The groundwater at 5.5 m to 6.0 m was also contaminated. The development and building approvals from the local government were not issued until the Environmental Protection Agency (EPA) issued suitability statements and the concurrence response to the local council permitting approval to start construction were issued. The following paper details the process which saw the issuing of these EPA responses and the pitfalls which were overcome by the developer.

CONTAMINATION ASSESSMENT

The contamination assessment was carried out in two stages before and after November 1998 by different organisations. The initial stage was undertaken by the tank removal contractor and the latter by Geo-Eng Australia.

Initial Contamination Assessment

Soil contamination

An assessment consisting of a series of soil analyses was undertaken during August, September, October and November 1998, by the contractor responsible for removing the last set of USTs. These showed hydrocarbon contamination of the soil with levels up to 486 mg kg^{-1} C_6-C_9, 3410 mg kg^{-1} C_{10}-C_{14}, 4970 mg kg^{-1} C_{15}-C_{28} and 3040 mg kg^{-1} C_{29}-C_{36}. These were above accepted standards. The benzene, toluene, ethylbenzene and xylene (BTEX) levels were less than the level of detection or below 1 mg kg^{-1} in two of the seven samples taken.

Groundwater contamination

In early November 1998, nine groundwater monitoring bores were established. Groundwater contamination was shown to have levels up to 27500 $\mu g\ L^{-1}$ C_6-C_9, 871000 $\mu g\ L^{-1}$ C_{10}-C_{14}, 1100000 $\mu g\ L^{-1}$ C_{15}-C_{28}, 2200 $\mu g\ L^{-1}$ C_{29}-C_{36}, 839 $\mu g\ L^{-1}$ benzene, toluene 485 $\mu g\ L^{-1}$, 1180 $\mu g\ L^{-1}$ ethylbenzene and 5730 $\mu g\ L^{-1}$ xylene. These were above accepted standards.

Latter Contamination Assessment

Geo-Eng became involved in December 1999 and began assessing the available data and evaluating the contents of the monitoring bores. Attention was concentrated on the groundwater as this had the potential to cause the greatest environmental harm off site. Free product was found on the surface of the groundwater in the bores at a thickness of up to 600 mm. This explained the high dissolved fractions of hydrocarbons found in the earlier sampling. Any soil contamination appeared to be confined to the site and was centred where the old USTs had been located.

Six additional monitoring bores (12, 13, 14, 15, 16 and 17) were constructed to determine the extent of contamination off the site and establish groundwater flow information. Constructed in February 2000, these bores indicated that the free product was limited to a uniform area of approximately 30-m diameter mainly on the site.

During the course of negotiations with the EPA, doubt was cast on the fact that the free product levels indicated in the bores were more a result of bore and soil features rather than the actual level of free product on the groundwater. In order to prove that there was limited free product, four additional 1.2-m diameter wells (Bores 18, 19, 20 and 21) were constructed across the centre of the field of contamination. Soil samples taken from these bores indicated

contamination levels of concern between 6 and 6.5 metres for bores 19, 20 and 21. Levels of up to 2000 mg kg^{-1} $C_{10} - C_{14}$ and 6400 mg kg^{-1} $C_{15} - C_{28}$ were recorded. BTEX levels were below the level of detection. After three weeks the free product on the water surfaces of these bores was negligible or at worst a very thin film. Levels of free product which developed in the 50-mm and 150-mm diameter bores were not evident.

The site layout, removed UST locations, bore locations (1 through 21) and proposed buildings for the shopping centre and a fast food outlet are shown on Fig. 1. This figure also indicates the extent of the free phase on the bores and the groundwater contours showing flow direction.

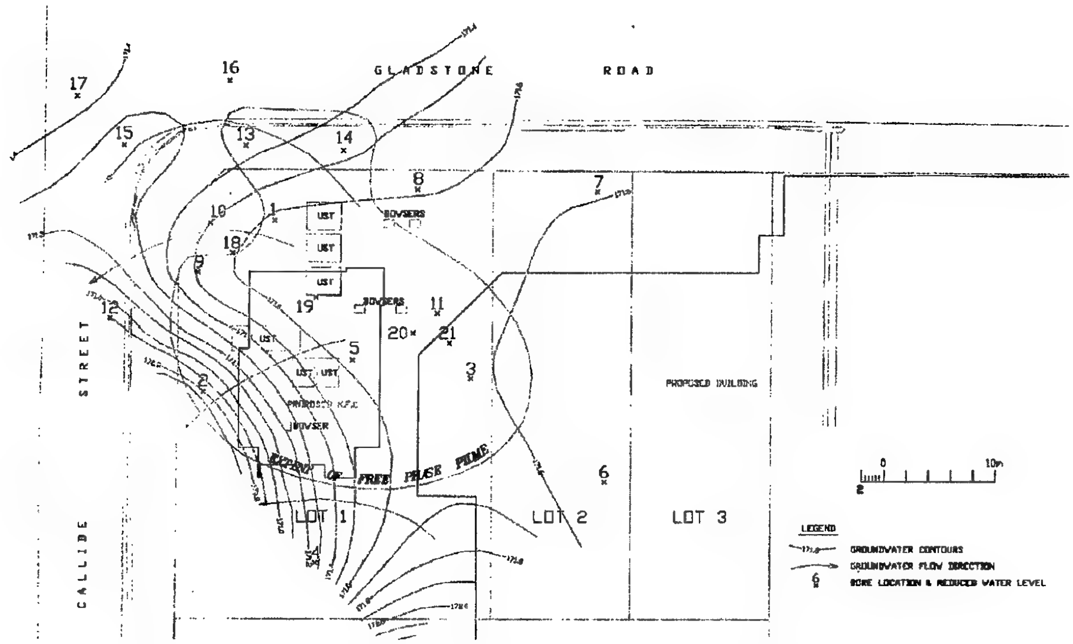

Fig. 1. Site plan showing UST locations, bore locations, proposed building locations, free product plume, groundwater contours and flow direction and street and lot locations

One of the major difficulties with assessment of the site is the nature of the geology. The top 5 m are clean soil fill or clays. At 5 to 6 m, a layer of river gravel and rocks appear across much of the contaminated zone. The rocks and gravel reduce in density and size as one moves away from the area where the USTs were located. It is not possible to use hollow flight augers as these refuse on the rocks which can be up to 300 mm diameter. Air or mud drilling can penetrate the rock layer but sampling for hydrocarbons is of no value. Hence soil sampling is difficult unless large diameter augers are used such as those taken from bores 18, 19, 20 and 21.

The site where the USTs and the deep contamination existed, had been excavated to at least 4.5 m and filled and compacted with clay material to a standard suitable for building construction. This created a barrier to any volatiles which may have existed. The volatile fraction was limited as the hydrocarbon contamination was in the heavier fractions and appeared to be diesel.

EPA REPORTING AND APPROVAL

In order for the shopping centre construction to begin, the local council had to obtain approval and conditions for the project from the EPA, as a concurrence agency under the Queensland *Integrated Planning Act 1997* (IPA). The site existed on the old contaminated land register due to its prior use as a service station. The EPA required that the contamination status of the site be determined and a SMP under Part 9B Division 5 of the Queensland *Environmental Protection Act 1994* (EPAct) be prepared and approved if any contamination of concern existed. All data was supplied to the EPA and a SMP developed. Problems arose when free product up to 600mm thick was recorded in the 50-mm diameter monitoring bores.

The EPA, prior to any consideration of approvals, required a human health risk assessment to be undertaken. Such a request was needed as a result of the existing contamination that posed a potential risk for employees through exposure to volatile hydrocarbons. This may enter the proposed fast food outlet building through cracks that may develop in the concrete slab.

A risk assessment of the data was conducted. It found that if, in the unlikely event, 1 m^2 of crack space per 32 x 32 m of concrete floor is realised, employees who work in the proposed fast food outlet building 8 hours a day, five days a week for 25 years under the exposure conditions described, could typically expect less than a 1 in 700000 chance of developing cancer from exposure to benzene vapour resulting of the contamination. Under these conditions, exposure to toluene, ethylbenzene or xylene was not considered an issue.

However, if air conditioning units were programmed to become active 45 minutes prior to employees arriving at work, the risk associated with soil-derived benzene would be typically reduced to less than 1 in 1.7 million.

The EPA approval required the owner of the site to ensure the following conditions are complied with in order to achieve the SMP objectives.

(a) To maintain a barrier between site contamination and site users.

(b) All underground services in the identified area of contamination must be constructed in trenches in which the services are surrounded by a minimum 0.5 m of uncontaminated fill.

(c) Site excavations in the area of contamination are to be monitored by an appropriately qualified and experienced member of a prescribed organisation in accordance with the EPAct. Excavation works are to immediately cease and the Administering Authority notified and advised of appropriate remedial action in the event that monitoring reveals offensive or noxious hydrocarbon odours at the work site and/or evidence of gross contamination.

(d) Site works relating to excavation, stockpiling, removal or disposal of soil or contaminated groundwater from the site must include provisions which ensure that the environment is protected. All contamination, safety and excavation processes are to be documented and records kept which demonstrate site management plan compliance.

(e) An air ventilation system is to be installed in buildings which are located above the area of identified contamination. The ventilation and air conditioning systems are to comply with Australian Standard AS 1668.2 (or equivalent) and are to be turned on 45 minutes prior to employee or customer occupation of the buildings and deactivated after the last occupant has left.

(f) A Workplace Health and Safety Plan which satisfies relevant obligations of the *Workplace Health and Safety Act 1989*, subordinate legislation or its equivalent is to be developed for all site work involved in the area.

(g) Contaminated soil must not be removed from the site without adequate sampling and prior approval from the administering authority under Section 118ZZF of the EPAct or equivalent.

(h) The owner must provide all contractors conducting building and associated works with a copy of this approved SMP prior to the commencement of works on site.

A groundwater remediation and monitoring program is to be installed and operated at the site to reduce the level of hydrocarbon impact on the groundwater. This program is to be supervised and reported to the EPA by a qualified and experienced member of a prescribed organisation in accordance with Section 118O of the EPAct.

Monitoring and Reporting

Records are to be kept of an annual inspection to ensure that the impervious barrier over the area of identified contamination site remains in good condition, any site excavations, contaminated soil disposal and site management plan compliance for review by the administering authority. As a minimum, groundwater from bores 1, 9 and 11 are to be monitored on a quarterly basis for TPH, BTEX and depth of phase separated hydrocarbon. To determine the extent of phase separated hydrocarbon, the bores must be left stand for at least two weeks prior to sampling.

A report documenting the results of monitoring, the status of the groundwater treatment system and site management plan compliance is to be submitted to the EPA annually.

REMEDIATION

A remediation plan as part of the SMP, has been developed based on groundwater extraction incorporating the depression of the groundwater levels and the cyclic flushing of the smear zone at the normal groundwater level. The water will be discharged to sewer under a trade waste license. It is expected that the flushing of the contaminated layer at the normal groundwater layer will progressively remove the contamination from the soil.

The groundwater extraction and treatment as approved by the EPA will include but not be restricted to the following.

(a) Two groundwater extraction bores (10 and 11) and eight monitoring bores (1, 9, 12, 13, 14, 15, 16 and 17) shall be maintained on and adjacent to the site as detailed on Fig. 1. The use of these bores especially with regard to extraction and injection, will vary depending on monitoring results.

(b) Groundwater including the thin layer of free product, is to be pumped from the surface of the groundwater by a top loading Enviroequip 90-mm pneumatic total fluids pump Model MVPIV. This pumping is to occur from a minimum of bores 10 and 11 to the treatment system. The system has a maximum pumping rate of 2000 L h^{-1} with the ability to control flow rates by controlling the inlet air supply rate, exhaust air rate and the flow through the rising main to the separator. Due to the low inflows of free product to the bores (only a thin layer on the water table) the bore is to be pumped at a low rate. During the recovery of the free product, the groundwater is to be treated by physical separation in a Sepa parallel plate separator Model PS-0-3-A-4-1 with treated water recharged into the site groundwater system at Bore 2, Bore 8 or Bore 10. The separator has a design flow rate of 3000 L h^{-1}.

(c) Once the existing thin layer of free product has become insignificant or free product no longer flows into the collection well; the groundwater is to be pumped at a higher rate to develop a steep hydraulic gradient towards the wells. The groundwater will be treated or discharged to sewer depending on the contamination concentrations and the obtaining of the relevant approvals from Council. Monitoring of the groundwater at the time will determine the pumping strategy.

(d) The groundwater extraction and treatment system must be designed, installed and operated so that it meets all Workplace Health and Safety, Council and EPA requirements.

(e) The groundwater treatment referenced above is to continue until the EPA advises otherwise and the SMP amended. To amend or stop the groundwater treatment program the owner is to submit a report to the EPA justifying the proposed changes in groundwater treatment. The report is to be prepared by a person who meets the requirements of s118O of the EPAct and the submitted report must, as a minimum, include results of analysis from relevant monitoring locations, details of the amount of product removed and justify why the separate phase hydrocarbon treatment system should cease or be altered. It should be noted that the EPA might require treatment of the groundwater dissolved phase hydrocarbon contamination following the separate phase hydrocarbon treatment. As a result, the submitted report is to also address the extent of dissolved phase hydrocarbon contamination and the necessity for further groundwater dissolved phase hydrocarbon treatment. If dissolved phase hydrocarbon treatment is required then a proposed treatment strategy is to be included in the report.

DISCUSSION

The contamination has occurred prior to 1973 and, due to inadequate assessment, not discovered until responsible evaluation of the site was undertaken in 1999 when the use of the site was proposed for change from a service station to a shopping centre. The inadequate evaluation of the potential contamination prior to proceeding with the project, caused significant delays and costs.

The progressive site assessment and the need for the EPA to satisfy itself that the risks were insignificant caused delays in obtaining building approval. Furthermore, the progressive gathering of all information needed and its interpretation by authorities created delays incurring additional costs and time.

Interpretation of data is crucial to the actions taken and the environmental approval process. In the case under discussion, the free product quantity was interpreted as being significantly greater and more significant than was the actual situation. On further evaluating the real thickness of the free product on the groundwater, it was found that the product was much thinner than the thickness in the bore. This is primarily due to the small amount of product and a thicker capillary zone above the groundwater level and the progressive build up of product in the small diameter monitoring bores (Fetter 1993). In fine-grained materials such as the clays on this site, the capillary zone may be thicker than in other materials. The large diameter bores which do not allow this effect to occur, validated that the free product layer was in fact very thin.

The remediation of the site is possible however difficult to validate due to the nature of the geology in the contaminated zone. As the groundwater is a good indicator of the level of contamination, a validation methodology will be determined based on an evaluation of the groundwater. The bores considered essential by the EPA are kept for remediation and future

monitoring. Unfortunately, other bores which would have been invaluable in determining changes in groundwater quality, were demolished due to site development.

According to the SMP, a remediation system and monitoring on at least a quarterly basis is required.

CONCLUSIONS

The project was delayed for over six months by: the inaccurate information supplied to the developer by a legal adviser; the progressive assessment of the site in an attempt to save short term costs; the interpretation of the data available; and the cautiousness and due process of the regulating authority.

The advice given to the developer initially lacked technical authority. As the site's previous use commonly results in contamination, a relatively inexpensive site assessment would have indicated contamination and saved the developer significant time and expense.

This case further highlighted the need to appreciate that contaminated site assessment and remediation is an evolving process and very site specific. While costs need to be contained, a restrictive approach in the hope of saving time and money can commonly result in the opposite. Once the initial contamination is discovered a process and budget should be developed and approved to allow a full investigation to occur.

By being able to carry out a full investigation and interpreting the data accurately, the environmental consultant can supply the regulating authority with a complete set of substantiated recommendations. This will allow the authority to minimise its work and not appear to be stalling the developer's progress.

Finally it is important to execute the requirements agreed with the regulating authority and adhere to the site management plan.

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Remediation of a Creosote-contaminated Housing Estate Martin Street Armidale NSW

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ABSTRACT: The Martin Street Armidale Housing Estate was constructed on the site of a former timber treatment plant which operated from 1968-1979. Creosotes and Copper-Chromium-Arsenic (CCA) were used as timber preservatives. The site was redeveloped as a housing estate in the late 1980s and 27 houses were established before contamination was identified in 1990. All development on the estate ceased but it was not until 1993 that the estate was vacated. Remediation of the estate commenced in 1998 and a large amount of buried infrastructure, including creosote pits, was excavated. However, only three of the houses were demolished. Validation sampling confirmed that the cleanup criteria was achieved and the site has now been signed off by an EPA-accredited auditor. The remediation strategy permitted the majority of the houses to be retained and thereby returned to the community as an asset.

KEYWORDS: CCA, contamination, creosote, housing estate, remediation, timber treatment

INTRODUCTION

The Martin Street Estate Armidale site is a benchmark for environmental planning. The site is a case study in both undergraduate and postgraduate environmental studies and has had a direct influence of the way in which we manage contaminated land. The 1998 Planning Guidelines released by the NSW Department of Urban Affairs and Planning makes reference to the Martin Street estate particularly in relation to development applications.

The assessment and remediation of the contaminated site presented technical challenges however the residents of the estate also experienced a number of challenges. They expressed justifiable concern for their health and the health of their families. Their situation demonstrates that we should not lose sight of the non-technical issues in the management of contaminated land.

BACKGROUND

The Martin Street estate is located on the northern outskirts of Armidale adjacent to Martin's Gully and the main railway line. A timber treatment site operated on the four-hectare site from 1968-1979. A railway spur delivered timber and bulk chemicals in rail tankers directly onto the site and an internal railway was used to transport logs to the treatment cylinder and around the site. Treated logs were stacked around the area and those most recently treated were placed on drip pads. A stormwater/spill collection system was located on the site and runoff directed to a saw dust filled dam across the road next to Martin's Gully.

Initially creosote was used to treat the timber but this was later augmented with copper-chromium-arsenic (CCA) compounds. Creosote is a heavy oil/tar material which can have a

characteristic odour of naphthalene or mothballs. Creosotes are made up of polycyclic aromatic hydrocarbons (PAH) some of which like benzo (a) pyrene are carcinogenic. CCA, also known as tanalith, gives timber such as treated pine a characteristic green colour. Both of these compounds are by definition toxic as they are used to prevent the biological action which causes timber to rot.

Timber was trolleyed into the treatment cylinder and impregnated with the chemicals which were stored in bulk above ground storage tanks. The treated timber was stored around the site prior to dispatch. The operation of the plant resulted in contamination of the site either through accidental spillages or excess chemicals dripping off the treated logs.

There was a history of spillages of both creosote and tanalith occurring at the plant. Local newspaper articles and reports by the local health inspectors revealed an ongoing problem with discharges to the adjacent Martin's Gully and on to Dumaresq Creek. Spillages were reported as early as one month after the plant was commissioned when thousands of gallons of creosote escaped down Martin's Gully, and again in December 1976 when approximately 15000 L of tanalith was accidentally released to Martin's Gully.

The plant ceased operation in 1979 and all surface structures removed and relocated to another town. The site was used for a variety of commercial uses and a maintenance shed which remained was used as a truck depot until the site was redevelopment in the late 1980s as a housing estate. The issue of potential contamination appears not to have been recognised until significant development had occurred. Creosote contamination was discovered on Lot 4 in the late 1980s and all development subsequently ceased but by this stage there were already 27 houses and units established on the estate.

A number of investigations were conducted by a variety of consultants and various remediation options considered. The debate and litigation regarding planning approvals and development continued while the residents of the Martin Street Estate found little relief from their concerns, fears and frustrations. Eventually the Commonwealth Government intervened in 1993 and assumed ownership of 33 of the 40 Lots. All residents were able to leave the estate and it has stood vacant since 1993.

EARLY INVESTIGATIONS

The actual extent of the contamination across the estate was somewhat difficult to establish because a considerable amount of earthworks has occurred during its development into a housing estate. Leveling of the site resulted in disperse low level contamination across the majority of the site and the removal of surface features made it difficult to identify potential hot spots.

Early investigations were a combination of both focussed and grid sampling. A chronology of aerial photographs was used to identify potential hot spots. An overlay of the current development over the location of former infrastructure confirmed that houses were constructed over the timber treatment cylinder and bulk chemical storage tanks.

The quality of the investigations varied and a subsequent review of the data identified anomalies in the sampling strategies and analyses.

A review of these investigations indicated:

(a) the major contaminants of concern were arsenic (As) and PAH;
(b) the PAH contamination away from the timber treatment cylinder was highly variable and there was no correlation between PAH and arsenic concentrations; and
(c) the majority of the contamination was in the initial 0.5 m other than in the area of the timber treatment plant where the contamination may be deeper.

The early reports resulted in remediation strategies ranging from a risk management approach to complete demolition of all dwellings and subsequent excavation across the estate.

DASCEM APPROACH

DASCEM was engaged by the Commonwealth Department of Finance and Administration to remediate the Martin Street Estate to a level that would permit best use of the site.

The DASCEM approach was to establish cleanup criteria that would permit residential use of the site while retaining as much of the housing as possible to maximise the return to the community.

Site Investigation

DASCEM did not conduct any additional site sampling but critically evaluated the data from previous assessments. A chronology of aerial photographs was used to identify the location of possible infrastructure and areas of potentially major contamination. Anecdotal evidence suggested that the site may contain underground fuel tanks and landfills. The University of New England was engaged to conduct a comprehensive geophysical survey across the most suspect areas which corresponded with the general location of the former timber treatment infrastructure. The detailed geophysical investigation included an electromagnetic (EM) metal detector survey, an EM conductivity survey, and a ground penetrating radar (GPR) survey of specific anomalies.

A number of anomalies were identified, however, the existing structures did not permit unambiguous interpretation of the survey data. Sufficient information was obtained to suggest the presence of buried infrastructure particularly in the area of the former treatment cylinder. The GPR demonstrated that the original surface of the timber treatment cylinder was approximately 1m below the current grade.

Cleanup Criteria

Cleanup criteria for the Martin Street site were based on considerations such as:

(a) soil characteristics;
(b) mobility of contaminants; and,
(c) health risk considerations.

A review of the arsenic concentrations reported in the earlier investigations indicated that 95% of the results were below 25.5 mg kg^{-1}. These results were significantly less than the 1997 National Environmental Health Forum (NEHF) standard residential health-based soil investigation level of 100 mg kg^{-1}.

Polycyclic aromatic hydrocarbon contamination in excess of the NEHF Standard Residential Criteria of 20 mg kg^{-1} was identified on specific Lots on the estate. Both the Australian and New Zealand Environment and Conservation Council (ANZECC) *Guidelines for the Assessment and Management of Contaminated Sites* (ANZECC/NHMRC 1992) and the NEHF set a PAH criteria of 20 mg kg^{-1} for residential use (NEHF 1996).

Therefore the need for remediation was primarily driven by the degree of PAH rather than arsenic contamination.

The proposed cleanup criteria of 100 mg kg^{-1} arsenic, 20 mg kg^{-1} PAH and 1 mg kg^{-1} benzo(a)pyrene were submitted to and accepted by the NSW Environment Protection Authority to enable residential use of the site.

Soil characteristics

The predominantly clay soil in the area reduce the migration of contaminants as:

(a) clay soils have low hydraulic conductivity resulting in minimal water and solute infiltration through the soils; and
(b) clay soils have the ability to bind strongly to cations.

Mobility of contaminants

The inorganic copper, chromium and arsenic present at the site all undergo cation exchange with the clay minerals. Once absorbed the cations are immobilised within the soil matrix and consequently pose little potential impact to the environment unless chemical changes such as altering the soil pH change the cation exchange relationship. Therefore the potential for natural movement of CCA in the soils is by physical means such as blowing or washing contaminated fines into cracks rather than solute transport.

Organic contaminants do not bind readily to clay minerals. The degree to which organic contaminants are stable within soil is primarily dependant upon the organic matter content of the soil. Consequently PAH are likely to be more mobile in soil than CCA but in absolute terms this movement is likely to be low.

Health risk assessment

A preliminary health risk assessment was conducted by AGC Woodward Clyde in 1991 based on US EPA criteria for evaluating human health risk at Superfund sites. The acceptable threshold was set at 30 parts per million (ppm) arsenic, 100 ppm copper and 20 ppm PAH. AGC Woodward Clyde concluded that the highly contaminated areas must be remediated and that an arsenic concentration range of 40 to 50 ppm in the soil would not result in an unacceptable health risk to the resident children. At the time of the assessment there was insufficient data available to develop similar guidelines for PAH.

The DASCEM cleanup criteria of 100 m kg^{-1} arsenic, 20 mg kg^{-1} PAH and 1 mg kg^{-1} benzo(a)pyrene were based upon the 1997 NEHF standard residential health-based soil investigation levels. These levels are based upon several conservative assumptions and are used to provide a tiered set of soil criteria for different exposure settings. The standard residential criteria adopted for the Martin Street remediation considers garden and accessible soil, home grown produce contributing less than 10% of fruit and vegetable intake, and no poultry. This criteria includes children's day centres, preschools and primary schools.

REMEDIATION STRATEGY

The remediation strategy was based on the following objectives;

(a) remediate the site to a standard which may permit an EPA-accredited auditor to confirm residential use of the estate;
(b) maximise the potential return to the community by demolishing as few houses as possible consistent with the above; and
(c) minimise any potential off-site impact to the environment and neighbours by controlling runoff and emissions.

A Community Consultation Committee comprising representatives from the Commonwealth, NSW EPA, Armidale City Council, DASCEM, emergency services, local environmental group, and neighbouring residents was established. The aim of the Committee was to keep the community informed as to the progress of the works and provide a forum to accept and provide feedback about the project.

Site Classification

The 4-ha site was classified into three contamination categories.

(a) Type A. Lots likely to be marginally in excess of the adopted cleanup criteria but satisfy NSW EPA criteria for disposal as class 1 solid waste. Contaminated soil not covered by houses or paving would be excavated to a depth of approximately 0.5 m. Additional excavation would be undertaken if validation sampling identified contamination in excess of the cleanup criteria.

(b) Type B. Lots likely to have contamination significantly in excess of the cleanup criteria. These are primarily the lots over the former timber plant infrastructure. Houses on these lots would need to be demolished to gain access to potentially buried infrastructure and underlying soil.

(c) Type C. Lots likely to have only minor levels of soil contamination and generally satisfy the adopted cleanup criteria. Type C lots comprise the majority of the estate and contamination is most likely due to recontouring of the area associated with the redevelopment of the site. Exposed soil on these lots and road reserves would be turned to a depth of approximately 0.3 m and top soil added to improve the amenity of the Lots.

Confirmation

In all cases, validation sampling would be conducted to ensure that the cleanup criteria were achieved. Additional excavation would be undertaken to either achieve the criteria, or a risk assessment identified that the residual contamination was effectively isolated.

An impervious barrier wall such as high-density polyethylene (HDPE) would be installed to effectively isolate non-Commonwealth Lots and prevent the possible migration of contaminants into remediated areas.

All excavated soils would be stockpiled on site, sampled and only authorised for disposal after the analytical results were fully evaluated. Soil which satisfied the Solid Waste Class 1 criteria would be transported on designated haul routes to the local landfill for disposal as top cover. Soil in excess of the solid waste class 1 criteria would be transported to a engineered designated remediation area (DRA) at the landfill designed to treat and contain contaminated soil.

Heavily contaminated soil would be treated in a thermal desorption unit to destroy the hydrocarbons, and metal contaminated soils would be chemically fixed prior to disposal.

SITE WORKS

A series of plans were developed, approved by the superintendent and implemented prior to site works commencing. These included an occupational health and safety plan, a remediation action plan, and sediment and stormwater runoff control plans.

All services likely to be disturbed during the works such as power, water and stormwater were terminated and removed.

The two houses scheduled for demolition were removed and as much as possible of the building materials were recycled. The exposed soil was assessed visually and stockpiled in different areas of the site dependant on its likely degree of contamination. No soil was removed from the site until the results of the analyses had been fully assessed.

The removal of the two houses revealed the first of a number of buried tanks containing creosote residues. All were within the area of the treatment cylinder and demonstrated that

little if any of the buried infrastructure had been removed when the plant was decommissioned.

A stormwater pipe associated with the plant was found to pass under a house which was not scheduled for demolition. A sewer camera was used to determine that this pipe terminated at another creosote pit directly under the house. This house was then demolished to permit access to the pit and to remediate the contaminated soil. A total of six tanks were eventually uncovered.

The buried remnants of the bulk decanting infrastructure and transfer lines at the former railway spur were also uncovered.

The areas of greater contamination generally coincided with the location of the treatment cylinder and infrastructure as identified from the aerial photographs. Excavations in these areas extended to a depth of approximately 2 m where fractured rock was encountered. The residual contamination was capped with a minimum 0.5 m of clay and the area surveyed to permit accurate representation on site plans. This approach was endorsed by the EPA-accredited auditor. Groundwater monitoring in the area did not identify any contamination in excess of the ANZECC criteria.

The site works confirmed that the majority of the contamination was close to the surface and primarily due to the recontouring of the site during redevelopment.

A minimum of ten validation samples were taken from each Lot following excavation together with samples from exposed boundaries and against house foundations to ensure the remediation criteria were achieved. An impermeable barrier would have been installed where the results showed contamination in excess of the cleanup criteria for any exposed vertical surfaces that could not be excavated further.

All excavated areas were backfilled with certified clean fill conforming to designated criteria. Services were reinstated, top soil applied and the area grassed and landscaped.

Approximately 5000 m^3 of contaminated soil conforming to class 1 solid waste was removed from the site. A further 1000 m^3 of more heavily contaminated soil was removed to the DRA for treatment. Regular testing of the soil at the DRA confirmed that the treatment was successful and this material was eventually disposed of as class 1 solid waste.

CONCLUSIONS

The Martin Street Estate is a seminal contaminated site. It has resulted in permanent changes to the planning process and the assessment of development applications in general.

The remediation of the site demonstrated that a thorough approach to both the technical and non-technical aspects of a project can produce a satisfactory outcome for all parties. A detailed and innovative site assessment coupled with a comprehensive remediation action plan resulted in minimum demolition and maximum return to the community. The development of a community consultation committee as a fundamental component of the remediation process ensured that the community had a forum to accept and provide feedback about the project

The remediation confirmed that little if any of the buried infrastructure was removed when the timber treatment plant was relocated. In some instances, houses had been constructed directly over creosote-contaminated pits.

A detailed and innovative approach to the project resulted in the successful remediation of the Martin Street Estate and brought to a close a remarkable chapter in the history of contaminated sites in Australia.

ACKNOWLEDGEMENTS

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The Holistic Role of New Woodland in Urban Regeneration and Site Remediation in the United Kingdom

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ABSTRACT: Planting trees is recognised to play an important role in countryside improvement but its additional importance in urban regeneration is not fully appreciated. In the UK, a continuing and consistent trend towards more building development has had limited success in the redevelopment of urban brownfield land despite government policies which target such sites. The problem arises from the low desirability of many brownfield and derelict sites that often have some degree of soil contamination from previous industrial uses. Woodland planting and established trees undoubtedly alter the aesthetic appeal of degraded land. Furthermore, all available evidence suggests that trees can be used to remediate contaminated land through phytostablisation or even through phytoextraction. There is an enormous potential role for trees to improve the environment. Woodland planting is now making its way into mainstream urban regeneration, forming a focus for low-cost and sustainable development.

KEYWORDS: trees, brownfield, contamination, multi-purpose forestry

INTRODUCTION

Until relatively recently the values we attached to trees and woods were very straightforward. In the countryside they essentially had a monetary value for timber whilst also being of value for outdoor recreation and a habitat for wildlife. In towns and cities, large aesthetically pleasing individual trees, usually associated with prestigious buildings, avenues or parks were all that was considered worth preserving. Large species of street trees have been frequently viewed as a potential hazard and liability by Local Authorities. These stereotypes are breaking down and there is growing recognition that trees and woods are an important and dynamic component of the urban fabric, providing a variety of benefits which increase the quality of life for millions of people. In this paper we argue that woodland planting may provide the most effective tools available for urban regeneration and towards achieving urban renaissance.

These benefits include energy conservation, with the shelter effect of trees saving up to 10% of energy consumption by either reducing heating or air conditioning costs of buildings (Heisler 1986). Tree roots also bind the soil, preventing erosion and improving soil stability. Urban forest tree canopies intercept and moderate the effect of heavy rainstorms, reducing storm water runoff and lessening the likelihood of flash flooding (Dunne and Leopold 1978). Trees also improve air quality - gaseous and particulate pollution is filtered by leaves. In Chicago, trees have been shown to remove 10.8 tonnes of the fine particulates, $PM_{10}S$, (which are associated with asthma) in an average summers day (McPherson *et al.* 1994). Tree belts, adjacent to roads can reduce noise levels by 6-8 decibels for every 30 m width (Leonard and Parr 1970). Trees also provide shade - skin melanomas caused by excessive exposure to UV radiation is the fastest growing form of cancer in England today (New 1999). They have a

role in stress reduction - the passive benefit to health of a wooded landscape has been demonstrated by the increased rate of recovery of hospital patients who have a view of greenery, as opposed to only buildings (Ulrich 1984). Furthermore, trees may have indirect benefits to the local economy. A 'green' aesthetically pleasing environment is recognised as a factor in attracting new businesses to an area and thus helping to create employment (Handley and Bulmer 1986). Several studies show that house prices are up to 18% higher where property is associated with mature trees (Morales *et al.* 1983).

The Potential for Woodland on Urban and Industrial Wasteland

Many initiatives have started up in the UK aiming to increase woodland cover from 5% to the current level of around 10%. These have in recent years been largely based on realising some of the benefits as outlined above rather than for their potential timber value. Cheap imports of timber from the USA, Scandinavia and latterly the Baltic States have greatly depressed timber prices. This state of affairs is likely to continue and has given greater impetus to developing new woodland for its many other benefits, focusing research and ultimately design on how best to achieve these objectives.

In December 1998 the British Government published its Forestry Strategy for England, *A New Focus for England's Woodlands* with similar strategies being planned for Scotland and Wales. The Strategy establishes the Government's priorities and programmes for delivering sustainable forestry in England over the next 5-10 years. One of the four key programmes within the strategy is *Forestry for Economic Regeneration.* Central to this programme is promoting the role of forestry in the restoration of derelict and former industrial land.

New woodland initiatives on the urban fringe in lowland Britain and increased interest in low-cost reclamation options for former industrial sites (brownfield sites) has resulted in much more extensive planting on contaminated soils (Glimmerveen 1996). To assess the significance and potential for this change in land use, we must first explore the nature and current stock of derelict and neglected land. The situation is a dynamic one, land moves into and out of the stocks of urban and industrial wasteland and has varying residence times within these stocks. If land is vacant for only a short period of time, such as some development land, then it can only be of limited use considering the time scales necessary to generate woodland.

National data on land use dynamics is very limited, but we can illustrate this movement with survey data gathered from Merseyside over a 20-year period (Fig. 1).

The most significant land use transfer over this period is of farmland moving into the development cycle. The stocks of derelict land (60% of which, nationally, can be considered contaminated (Perry and Handley 2000) and also neglected land being relatively static. These data are specific to a small area of Britain around Liverpool, where the local economy is particularly weak, but are consistent with a broader and more expansive trend towards urbanisation elsewhere in the UK. Whilst it is a very high priority to recycle land for urban and industrial use, especially where traditional industries such as coal and steel have declined, on many sites this is either inappropriate or just too expensive. Here, woodland may offer a cost-effective alternative, creating an attractive setting for both residential areas and industry, ultimately assisting in the process of urban regeneration.

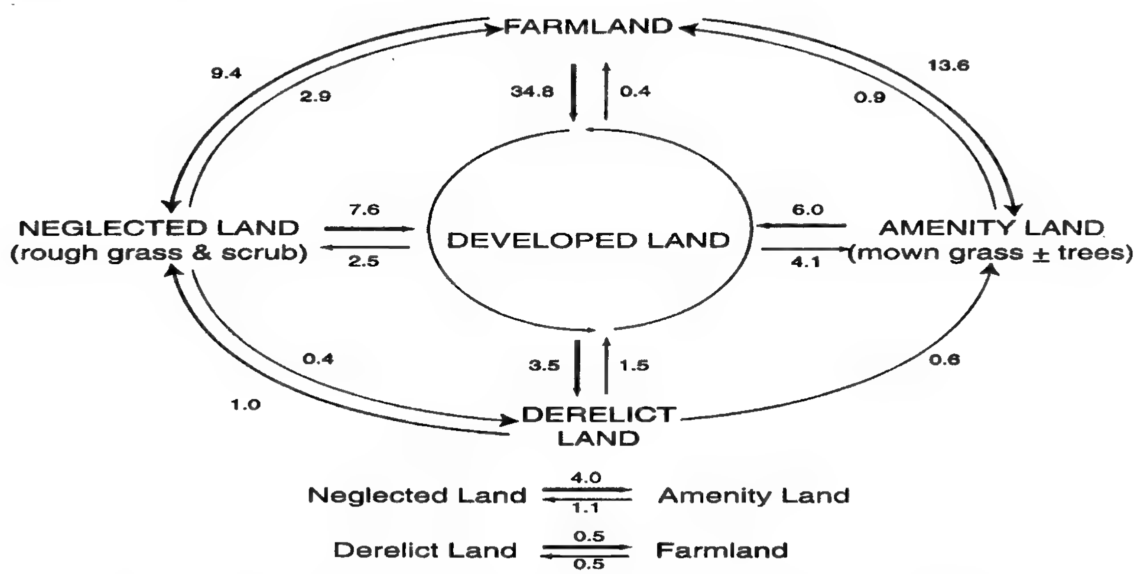

Fig. 1. Cycle of land use change (km^2) from 1960-1982 in Merseyside county (total area – 663 km^2). Source: Joint Countryside Advisory Service, Mersyside, UK 1988

It seems likely that in the future, the process of reclamation will be matched by new land becoming vacant through mineral workings, waste disposal and changes to the nature of the British industrial base (Perry and Handley 2000). Although it has been estimated that a high proportion of vacant land can be considered contaminated, very little information exists in the public domain of the extent of contamination and therefore also on the rate of change as contamination is either created or cleaned up. The cost of establishing precise geographical site-based information on levels of contamination is high. These added survey costs and the issues of establishing historical liability for the contamination tend to isolate this type of land from the development cycle without publicly funded assistance to offset the site investigation and remediation costs (POST 1993). Whilst this is obviously undesirable in terms of sustainable urban renewal on so called 'brownfield land' it is an opportunity for new woodland creation in urban areas. It is also an opportunity for woodland creation and development to have a somewhat symbolic relationship. Assuming levels of contamination do not prejudice the use of the woodland as an amenity or actually prevent tree growth (as discussed later), the use of part of a development site such as the site perimeter for new woodland will have a number of benefits. The advanced planting will provide shelter, screening and many other benefits, as previously described, to the development. The land designated for woodland will require a much lower level of site remediation (if any) than for the development and thus reduce costs. From the developer's point of view it may also be expedient to introduce this perimeter landscaping at an early stage (which may be required as a planning condition anyway) to improve the attractiveness of the site to potential clients.

PLANTING TREES ON CONTAMINATED LAND

Current Guidelines

Concerns are often raised by those concerned with land development about the toxic effects of soil pollution, but it is increasingly apparent that trees can survive and grow on land containing levels of contamination a factor of 10 or even 100 times higher than current

guidance values (Dickinson *et al.* 2000). The most frequently used guidance in the UK is that produced by the Interdepartmental Committee for the Redevelopment of Contaminated Land (ICRCL, 1987). The trigger and threshold concentrations used here partly originate from an attempt to predict toxicology limits for clean soils that are under threat of being progressively contaminated. As with many countries (Sheppard *et al.* 1992) UK regulation and legislation concerning heavy metal contamination is based on total metal concentrations in the soil. These criteria are excessively conservative and actually address a worst case scenario; meaning effectively that insoluble, non-reactive and non-bioavailable forms are classed as hazardous as are highly soluble, reactive and biologically mobile forms (Sauve *et al.* 1996). Little quantitative and qualitative assessment is taken of the total and free ion concentration in the soil solution, even though these are likely to determine the bioavailability of metals and their potential toxicity.

Toxic Concentrations and Bioavailability

The point at which heavy metal contaminants in soil become phytotoxic is notoriously difficult to predict. A number of physical, chemical and biological variables affect the bioavailability to the plant and its potential toxicity. No single method of soil testing has been found that can accurately predict the bioavailability portion of soil metals (Thornton 1999). The levels available in solution for potential uptake by roots is affected by many physical factors including precipitation, leaching, levels of organic matter, clay minerals, iron, manganese and aluminium oxides, pH and several others (Mench *et al.* 1998). Another significant factor may well be the type of mycorrhizal association or even particularly tolerant genotypes. To complicate matters further, uptake is also influenced by interactions among metals, the age and vigour of a tree as well as mycorrhizal/root associations and soil invertebrates (Punshon 1994).

Site-based Evidence

Examples of trees that have naturally colonised sites with exceptionally high levels of multiple metals are very common (Dickinson *et al.* 1991, Watmough and Dickinson 1995, Glimmerveen 1996). The mechanisms by which they can cope, and even thrive, in these conditions, notwithstanding the bioavailability issue, can be by avoidance i.e tree roots can actively forage towards less contaminated zones of soil (Turner and Dickinson 1993), or by effectively shutting off growth and waiting for more favourable growing conditions (Watmough 1994). Metal tolerance to zinc and lead has been identified in populations of birch and willow (Denny and Wilkins 1987, Eltrop *et al.* 1991). Eltrop *et al.* (1991) found *Salix caprea* (goat willow) growing in soil with total concentration of 17000 μg Pb g^{-1} (with NH_4-HOOAc extractable concentrations of 4000 μg Pb g^{-1} and *Betula pendula* (birch) in soil with total concentrations of 29000 μg Pb g^{-1} (extractable concentrations 7000 μg Pb g^{-1}).

Phytoremediation

Trees have the potential in the future to be used to either stabilise contaminants in the soil by rendering them immobile (phytostabilisation), or to remove contaminants by accumulating heavy metals within the woody tissue (phytoextraction). These two strategies are illustrated in Fig. 2.

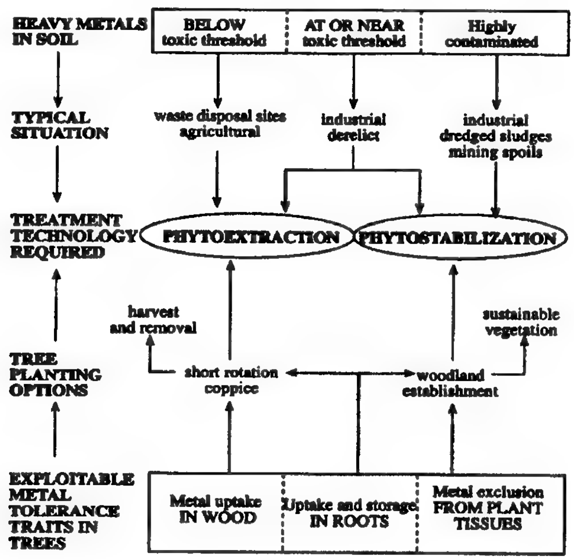

Fig. 2. Phytoremediation Strategies

The two strategies represent quite opposite approaches to soil reclamation but earlier work using laboratory and glasshouse trials (Dickinson 1996) have shown both options to be feasible. Trees survive toxic metal stress through tissue exclusion or by uptake and tolerance of high tissue concentrations of metals. Some willows (Salix spp.) growing on industrially-contaminated soils for instance, have recorded woody tissue concentrations of Pb, Cu, Cd and Zn in excess of 250 mg kg^{-1} dry weight (Dickinson 1996). Willows are also highly productive in terms of biomass, so in the context of short rotation coppice, a measurable reduction in soil metal levels is theoretically possible over a period of several harvests. Phytoremediation represents a potentially low cost, low technology and sustainable solution for low value metal-contaminated land.

RECOMMENDATIONS

Risk Assessment

The process of remediation is carried out within a risk-based framework, using risk assessment and risk management to make decisions and to take appropriate action to deal with contamination (Cairney 1995, Kearney and Herbert 1999). In relation to tree planting strategies, the risk assessment of greatest environmental importance is not what impact contaminants will have on trees but what effect will be caused by planting trees. Currently, human health issues largely drive the current UK 'dig and dump' strategy for reclamation of contaminated land. Planting trees may pose risks to both human health and the wider environment, through increased mobilisation of toxic chemicals, leaching to groundwater and contamination of the terrestrial food chain. This is less likely to be an issue with toxic organic chemicals that tend to break down into less complex harmless molecules. Established trees also limit the rate of flow of water and therefore the mobility of chemicals through soil. Risks to human health from planting trees through upward movement of metal contaminants such as Cu, Ni, Zn are negligible. However, despite this, risks to other organisms in food chains and to important ecological processes can be caused by mobilisation of these 'phytotoxic' elements. Implications of upward movement of zootoxic elements (e.g. As, Cd, Cr, Pb, Hg, Se) may have more serious implications to human health. Without longer-term studies it is

impossible to predict whether trees will alter patterns of mobility of potentially toxic chemicals but there is little evidence to suggest this may happen. In fact, planting trees is likely to lead to less upward mobility of heavy metals into food chains (Glimerveen 1996)

Working Guidelines

In view of the facts that trees can grow on highly contaminated sites and that there is no completely unambiguous method for determining the bioavailable fraction of metals in soils, clearly there is some need for practical guidance on what is an acceptable risk when considering new tree planting.

Even when that risk is assessed to be unacceptable amelioration techniques can be employed to mitigate these risks. The addition of calcium carbonate in a form such as crushed limestone will raise the pH of the soil and therefore help immobilise contaminants. Similarly, the spreading of an organic material such as sewage sludge (from a non-industrial source) may prove to be beneficial. In both cases, incorporation of the added material into the surface layers of the soil will give a more efficient and universal moderating effect. Repeat applications, particularly when liming, may be necessary to maintain the desired site amelioration.

Putting aside the potential for soil amelioration and the fact that most available soil metals will probably become bound outside the roots or in the cell wall, working guidelines for trace elements contamination levels suitable for tree planting have been put forward by Dickinson *et al.* 2000 (Table 1).

Table 1. Proposed tolerated values (mg kg $^{-1}$) for total concentrations of trace elements in soils and plant foliage that should be considered suitable for tree planting

Element	Soil [1]	Leaf [2,3]
Cu	600	100
Zn	3000	900
Ni	250	220
B	30	100
Cd	15	200
Cr^{6+}	600	
Cr (total)	1000	30
Hg	20	8
Pb	2000	300
As	80	20
Co	240	50
Mo	200	50
Se	50	40

1 Values are highest concentrations from Table1, largely relating to remediation values (Eikmann and Kloke 1991) or ICRCLE (1987) values for parks, playing fields and open spaces

2 Values are the range of upper critical concentrations from Table 3 (Kabata-Pendias and Pendias 1984, McNichol and Becket 1985, Alloway 1995, Power and Woods 1997)

3 Newly opened leaves should be sampled and washed on collection

CONCLUSIONS

The UK is one of the most densely populated countries in the world and 10% of its population live in towns and cities. The benefits trees can bring to urban areas are many and varied and increasing woodland cover is making its way into mainstream urban regeneration, institutional frameworks and policy documents such as the England Forestry Strategy (Forestry Commission 1998). To achieve these policy objectives the opportunities need to be realised where they exist. In a climate of complex and dynamic land use changes, a move towards sustainable development and conserving scarce land resources, new tree planting on derelict land and vacant land is both pragmatic and cost effective. This is particularly relevant where so often the land is deemed to be contaminated and remains abandoned and derelict for reasons of costs of redevelopment or fear of litigation. Current guidelines on risks to plant health from contaminants is extremely conservative and there is clearly a need for improved guidance for tree planting on brownfield sites. Whilst we lack a complete understanding of the effects of tree planting on the speciation, mobility and dispersal of toxic chemicals into the wider environment, there is no current evidence of detrimental or harmful effects (Dickinson *et al.* 2000). There is, however, an enormous potential role for the use of trees to improve the environment.

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Balancing Ecology and Archaeology: A Case Study - Block 10 Hill, Broken Hill

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ABSTRACT: The environmental remediation of sites such as former mining and industrial operations, must also by law (in some States such as NSW) include an evaluation of the heritage significance. This case study details the challenge of the remediation of a contaminated site whilst considering the environment (both ecological and human health) and archaeologically significant ruins. The case study presents the results of a bi-disciplinary study (heritage and environmental assessment) of the Block 10 Hill historic site in Broken Hill, New South Wales. Normandy Ltd (Normandy) undertook the remediation of Block 10 Hill with the assistance of an environmental consultant, OTEK Australia Pty Ltd (OTEK), and an archaeological consultant, Austral Archaeology (Austral). The work was undertaken to address contamination issues (possible ecological and human health effects) and archaeologically significant ruins. Concentrations of lead, zinc and cadmium above environmental and health investigation levels exist on the site due to the former mill operation. This paper details the consultative community liaison, development and implementation of the remediation action plan.

KEYWORDS: ecology, archaeology, Broken Hill, remediation, mining, heritage

INTRODUCTION

Normandy engaged OTEK and Austral, to jointly develop a remediation action plan for the site. This included balancing the remediation of exposed residual tailings dams and the archaeologically significant ruins. Possible exposure pathways from the contaminated material on the site included: ingestion, dermal absorption and inhalation. Monitoring in the early 1990s indicated that inhalation was not an exposure pathway as the lead particles were not of a size which could be inhaled. Levels of lead in air were significantly higher in major NSW cities when compared to Broken Hill, due to lead in petrol. A drain was located adjacent to the site to which the site drained. Runoff water which drains towards South Road is directed to downstream storage dams or via a bypass to a series of sediment ponds/wetlands. It should be noted it is estimated that 20 million tonnes of high grade lead and zinc eroded from the orebody prior to its discovery and that the Broken Hill area has naturally occurring elevated background levels of lead and zinc.

The Block 10 Hill historic site is part of Consolidated Mining Lease CML7. The specific boundaries of the site were not defined and site bounds were interpreted from aerial photographs and mining lease plans. The site reconnaissance was undertaken between 11 and 13 August 1998.

BACKGROUND

The following sections provide background information pertinent to the understanding of the assessment.

History

The BHP Block 10 Co. Ltd was floated as a separate company by BHP in 1888. Block 10 was one of the original Broken Hill leases and is situated roughly at the centre of the line of lode.

A concentration mill was erected on the lease in the 1890s but due to subsidence it had to be relocated. Tests were carried out on the adjacent Block 10 Hill (the subject of the current investigation) to determine if there was ore below it (and hence its likely future stability). No ore was found and the mill was constructed there in 1903. An aerial ropeway, the first in Broken Hill, was also constructed. The aerial ropeway transported ore about 600 m from the mine to a large storage bin above the mill, which could treat 3500 tons of ore per week.

The new concentration mill commenced operations in 1904. The mill was modified and extended throughout the early years and continued operations until 1923. In that year the parent company purchased the subsidiary and closed down the mine and mill. The mill never reopened but the mine (not in the subject area) was reworked by Broken Hill South Ltd between 1946 and 1960. Production totalled 2.5 million tons of ore worth £1.5 million. Dividends were paid up until 1923.

In 1993 the NSW Department of Mineral Resources (DMR) commissioned Austral to undertake a preliminary archaeological survey of the Block 10 Hill. This request was in response to heavy rains washing away residual tailings and exposing extensive footings and foundations of the former concentration mill. The DMR (in conjunction with Broken Hill City Council (BHCC) and Normandy) sought advice as to the heritage significance of the remains before any mitigative or rehabilitation works were undertaken. The resultant report established that the remains were highly significant and should be conserved.

Subsequently, the bulk of the tailings were removed from the Block 10 Hill by Normandy leaving the historic remains exposed. BHCC then established a walking trail and lookout on the hill as part of a heritage trail around the city and along the Line of Lode. Static interpretation comprising historic photographs and explanatory text on enamel signs were erected at the lookout. Two replica aerial ropeway towers were also erected.

Zoning and Intended Use of the Site

The Block 10 Hill is zoned under the BHCC for "mining" and no development (for example residential) is permitted. The Block 10 Hill site is also listed in the BHCC Local Environmental Plan (LEP) as a heritage item (No 188). It is intended that the site will be maintained for its heritage values. An existing lookout with static signage will continue to be utilised. It is not intended to provide further access in or around the ruins for heritage interpretation purposes as most of the ruins are best appreciated from the existing vantage point of the lookout area.

While the significance of the site is recognised by its inclusion in the LEP, the site is also covered by the relics provisions of the NSW Heritage Act. Under these provisions, any archaeological relics over fifty years old must not be excavated or disturbed without the prior approval of the NSW Heritage Council.

Consultative Process

Liaison was undertaken with representatives from Normandy, DMR, NSW Environment Protection Authority (EPA), BHCC, Broken Hill Water Board, Department of Land and Water Conservation, Broken Hill Environmental Lead Centre (BHELC), Austral and OTEK. Consultation was undertaken via the Mine Rehabilitation and Environmental Management Plan process that is managed by the DMR. Some of the issues discussed included:

Land Use

The BHCC wished to preserve the heritage aspects of the site and encourage tourism.

Environmental

The EPA requested that the intended use of the site needed to be established in order that appropriate environmental management of the site could be implemented. Based upon a hypothetical scenario of passive tourism the following environmental issues were considered with respect to rehabilitation works:

(a) residual tailings dams exposed by a drainage channel adjacent to South Road;
(b) dust generation from residual tailings;
(c) sediment transport off site during storm events; and
(d) fencing to restrict access to the site.

Exposure pathways from contaminated material on the site included ingestion and dermal absorption. Rehabilitation of the site would need to remove the source of contamination, the exposure pathway and/or the receptor.

Community Concerns

A local community representative supported the heritage use of the site and expressed concern regarding public exposure to the tailings and dust from the site.

Community Use

The community use the lookout established at the site to observe the general Line of Lode area and the archaeologically significant ruins at the site.

HERITAGE

Location of Historic Features

The historic features are mainly located on the top and upper southern and eastern sides of the Block 10 Hill although major structural ruins are located right down the eastern face of the hill. The relocation of South Road to its existing position (previously it was located further to the east) means that it has been built over some old slimes dumps. These may or may not have surviving structural elements.

Ruins at the site have been tentatively identified with the aid of a 1908 company plan and historic photographs. These include the:

(a) ruins of the large ore storage bin foundations and unloading station for the aerial ropeway – located adjacent to the lookout;
(b) the footings for one of the aerial tramway pylons - located to the east of the lookout;
(c) ruins of the concentration mill building – located to the immediate west and south of the lookout;
(d) ruins of settling tanks – the bases are located to the south of the lookout;
(e) ruins of the vanner house extension - located on the lower eastern slope; and

(f) ruins of concrete bins - the bases are located to the north of the vanner house extension almost immediately below the lower pylon.

Nature and Condition of Remains

The nature of the historic remains at the site mainly consist of low level structural ruins including floors, walls, foundations and footings, retaining walls, protruding structural bolts, timber linings (in sluices and pits), displaced timber posts as well as some portable relics of the former plant or equipment. Most of the structural elements are constructed of local stone, or brick and stone, or concrete. Both un-reinforced Portland cement based concrete and rough lime concrete were noted at different points.

In general terms, the previous cleanup of tailings extended down to former floor levels (within structures) and former operational ground levels in other areas. Some of the concrete floors have been rendered invisible since the cleanup as they have acquired a thin layer of redeposited tailings or other material.

It is likely that there are more historic features lying buried in and around the exposed features. These are likely to be pits, channels and foundations. The upper surfaces or upper extremities of such features were noted at several places in the site inspection.

The condition of most of the structural ruins appears to be fairly stable. Most of the walls which are constructed of stone would benefit from the application of a lime mortar capping (colour matched) to prevent weather ingress. The low local rainfall, however, means that deterioration will generally be slow even without capping. The brick elements (mainly quoins to stone walls but also incorporated into some free-standing footings) are generally in poor condition through the uptake of salts and consequent fretting. These are generally beyond help without total replacement. Some drainage works to prevent erosion and redirection of water away from these structures would assist in their long-term survival. The concrete floors and foundations are generally in reasonable condition and do not as a rule appear to require conservation treatment. The timber elements are generally either *in situ* and largely still buried (such as the pit or sluice linings) or totally exposed and displaced (such as various oregon and other timber beams, posts etc). All appear to be in reasonably sound condition and no treatments are required at this time. The portable relics, all of which are made of steel or iron, also appear to be in reasonable condition. Again the low rainfall should ensure very slow deterioration and no conservation treatments are recommended at this time.

During the survey it was noted that tourists to the site were climbing on the largest and most conspicuous structural features - stone and/or concrete wall foundations. In the case of the stone walls, this will dramatically increase their rate of decay. Fencing of the walkway through the site is not proposed, however signs requesting people to keep off the ruins are recommended.

Areas of Heritage Significance and Site Rehabilitation

Based upon the site meetings, historical information and field assessment, the following was concluded:

(a) All of the area containing structural ruins of the concentration mill and associated plant was considered to be significant and should be conserved. This area was defined on site in collaboration with the contamination consultant;

(b) It was determined in discussions between the consultants that there was no need for heritage structures or features to be impacted by the proposed remediation treatments. It was acceptable for some drainage or anti-erosion measures to be

instituted on historic surfaces such as bunds on floors or around features. Overall there was no adverse impacts on heritage resources;

(c) The residual tailings and locations where tailings have been removed were considered significant for the information they provide on historic treatment processes used at the site. The possible health or ecological risk however was considered of over-riding importance and these areas were rehabilitated. Either removal of the tailings back to bedrock, or the covering the tailings with mullock were considered suitable solutions to the problem and were compatible with the industrial heritage of the site.

Opportunities for Interpretation of Heritage Sites

The lookout at the site provides community and tourist access to the archaeologically significant ruins.

Contamination

Issues associated with the contamination were assessed by OTEK. The following sections describe these issues.

Existing Soil Concentrations

OTEK reviewed a draft report dated 23 March 1998 prepared by DMR titled "NSW Department of Mineral Resources Sampling Report for CML 7 – Block 10. The results of the sampling program indicated that concentrations of lead, zinc and cadmium above environmental and health investigation levels exist on the site due to the former mill operation.

Areas of Concern

The environmental areas of concern on Block 10 Hill are listed below and rehabilitation options adopted are shown in Table 1.

(a) Former tailings dams adjacent to South Road
(b) Sewage Sludge Areas
(c) Erosion gullies
(d) Catchment area near Ryan Street
(e) Restriction of public to the general site area
(f) Heritage foundations
(g) General Site

SITE REHABILITATION

The Site Rehabilitation performed balanced the needs of all parties involved whilst still addressing the heritage and environmental assessment. Specific details are provided below.

Surface Hydrology and Soil Erosion Control Measures

Normandy engaged John Miedecke and Partners Pty Ltd to prepare a stormwater management plan. This included the design of a stormwater runoff control system that addressed measures to prevent erosion and transport of contaminated sediments off site. The

basis of the control system included diversion of surface waters into on-site storages so that the waters were retained and evaporated, or at least have a period of initial settling, prior to spillage during high rainfall events. Runoff from upslope areas flowing over areas of exposed sediments were diverted to reduce surface flows and areas of concentrated flow, were diverted to either bedrock or rock lined spillways. The detailed design also involved identifying three specific catchments over the site and the appropriate storage volumes required.

Table 1. Ecological and Human Health Concerns and Remedial Works Completed

Area	Ecological and Human Health Concerns	Completed Remedial Works
Former tailings dams adjacent to South Road	Sediment transport off site during storm events. Drainage channel eroding through tailings dams.	Relocation of tailings at the north side of South Road Drain. A stable bank along the drain (at the site boundary) covering the north bank and adjacent flat area with mullock. Placement of mullock in the eroded gully area. Flat area adjacent to Tamrock covered with mullock.
Sewage Sludge Areas	Dust generation.	Levelled and covered with mullock.
Erosion gullies	Sediment transport off site during storm events and dust generation.	Sediment traps/erosion control measures constructed. Limited Coverage with mullock.
Catchment area near Ryan Street	Dermal contact by children playing in the area. Sediment transport off site during storm events and dust generation.	Sediment traps/erosion control measures constructed. Coverage with mullock.
Restriction of public to the general site area.	Dermal contact by children playing in the area. Dust generation by trail bikes and persons walking through site.	Mullock heaps were located in strategic positions to restrict access to vehicles and trail bikes.
Heritage foundations	Dust generation. Access to these areas by the public will be restricted.	Loose tailings material was removed and disturbed areas covered around heritage items with 100mm quarry road base material. Areas with concrete were not covered
General Site	Dust generation. Sediment transport. Contaminated water.	The rehabilitation works were carried out in a manner that minimised air borne dust.

CONCLUSION

The environmental remediation of Block 10 Hill by Normandy demonstrates that successful rehabilitation of a contaminated site whilst considering the environment (both ecological and human health) and archaeologically significant ruins can be achieved. The remediation process was also part of an extensive consultative process undertaken by Normandy including government departments, government authorities, environmental and community representatives and specialist consultants.

Similar heritage assessments of industrial sites prior to remediation have been undertaken by Austral on 1930s open cut coal mining sites near Lithgow in NSW, at the 1920s Chillagoe copper/lead smelter in far North Queensland, at the former 1890s North Mount Lyell copper smelters in south western Tasmania, at all the major gold mines around Tennant Creek in the Northern Territory, and at all the mines along the entire Line of Lode in Broken Hill. In many cases there is a conflict between the desired heritage conservation outcomes and the necessary remediation measures. Generally this is overcome by a consultative process involving all the relevant stakeholders and specialist consultants. Solutions often include ranking the relative cultural significance of heritage items on a site, undertaking the minimum acceptable remediation works and thus minimising impacts to the heritage items, covering contaminated areas rather than removing them (to control dust and water borne movement of contaminants), and restricting or totally banning access to the contaminated areas.

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When is it Acceptable to Leave in Place Sources of Ongoing Groundwater Contamination?

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ABSTRACT: One of the challenges of contaminated site management is achieving a balance between environmental protection and the financial cost of cleanup. Regulatory policy seeks to remove ongoing sources of groundwater contamination, however, it is often difficult to develop a strategy that fully considers these potentially opposing issues. Regulatory authorities have introduced the concepts of "practicable cleanup" in Victoria and "significant risk of harm" in NSW. The practical application of these concepts in resolving groundwater problems and defining cleanup requirements is still developing. Herein, important questions regarding site cleanup decisions are outlined using two case examples. It is important that policy objectives be tempered with practical issues, such as human and environmental risk, future site uses, technical feasibility of cleanup, and the cost of remediation. A primary objective of this paper is to discuss approaches for balancing technical needs with regulatory policy.

KEYWORDS: site cleanup, significant risk of harm, technical impracticability

INTRODUCTION

Environmental regulatory authorities have the responsibility to protect the environment and to strive towards cleaning up contamination which can adversely affect beneficial uses of land and groundwater. In order to guide their decision making process, a number of environmental legislation, regulations, policies and guidelines have been drawn up. In Australia the environmental authorities have generally adopted a risk-based approach towards the management of contaminated sites. This risk-based approach allows for a flexible management strategy that is not prescriptive in nature, with the overall objective of ensuring that land and groundwater is suitable for its proposed use (either current or future).

A difficult problem that the regulatory agencies face is how to achieve cleanup solutions which achieve a reasonable balance between remedial expenditures and net environmental benefits. This is particularly so in the area of contaminated sites remediation, where it is clearly desirable to cleanup contamination so that the possible range of uses are protected. However, in some cases the cost to achieve this ideal can be extreme. The problem is then how to determine and allow a compromise solution reflecting a reasonable expenditure for the environmental benefit obtained, and which does not set precedents that undermine the system that has been set up.

Towards this end, regulatory authorities generally allow the use of risk assessment to avoid unnecessary prescription in the use of published guideline values. EPA has introduced the concepts of 'practicable cleanup' in Victoria and 'significant risk of harm' in NSW. The practical application of these concepts in resolving groundwater problems and defining cleanup requirements is still in its early days.

This paper discusses the difficult problem of determining when groundwater contamination and sources of groundwater contamination need to be cleaned up, in the context of two case studies designed to highlight specific environmental issues.

THE ASSESSMENT OF RISK ASSOCIATED WITH GROUNDWATER CONTAMINATION

The use of risk assessment has been endorsed in principle by most regulatory authorities in Australia. However, its use has been limited and there is still uncertainty regarding the basis of risk assessment as well as the risk-based decision making process. Development and implementation of a risk-based approach is critical to the success of the complex environmental problems discussed in this paper. Risk assessment allows for an evaluation of whether the contaminants at a site are likely to pose a threat to human health or the environment in either the short term or the long term. Assessing the potential risk associated with groundwater contamination requires a thorough review of a number of site-related issues, including:

(a) nature and extent of contamination,
(b) site geology and hydrogeology,
(c) current and future site use plans,
(d) ecological setting and habitats,
(e) relevant exposure routes,
(f) potential groundwater connections with surface water bodies or other off-site receptors,
(g) regulatory requirements,
(h) local land and groundwater use.

WHEN HAS CLEANUP OF GROUNDWATER OR A SOURCE OF GROUNDWATER CONTAMINATION BEEN CARRIED OUT TO THE EXTENT PRACTICABLE?

It is a common situation that cleanup of the most easily accessible sources of groundwater contamination has been carried out, but some residual contamination remains either at depth or in relatively small and localised areas that is difficult and costly to remove. This scenario typically presents itself in settings where there is complex geology (e.g., fractured basalt, faulting) and with chemicals denser than the groundwater (i.e., dense nonaqueous phase liquids, DNAPLs). It may be very difficult to define the extent of contamination for sites like this, which tend to have localised pockets of contamination rather than a defined plume.

> Example for consideration: Gasworks site where the geology comprises clay underlain by fractured rock, where cleanup has been carried out and tar-affected soil has been removed, but some tar remains in fractures in the rock and forms an ongoing source of contamination of shallow groundwater. Cleanup of groundwater has not been attempted, other than to reduce future groundwater impacts as a result of the soil cleanup. Groundwater is used for domestic and stock use in the region.

In general, the regulatory agencies attach great importance to removing sources of contamination. The Victorian EPA has introduced the concepts of 'no unacceptable risk' and 'cleanup to the extent practicable' in their State Environment Protection Policy (SEPP) (Groundwaters of Victoria):

(a) Clause 18: "*where non-aqueous phase liquid (NAPL) is present in an aquifer, it must be removed unless the Authority is satisfied that there is no unacceptable risk posed to any beneficial use by the NAPL*".

(b) Clause 19: allows that a polluted groundwater zone can be identified by the Authority as having existing groundwater contamination that precludes one or more beneficial uses that would otherwise apply to that groundwater. In such zones the Authority will require "*groundwater to be cleaned up to the extent practicable in order to move towards the objectives prescribed in this policy to protect beneficial uses*".

While the decision basis is still evolving, important questions need to be considered.

Has there been an effort to cleanup the contamination or its source? There is a stronger case for concluding that cleanup has been to the extent practicable if cleanup has been carried out, and this cleanup has provided direct evidence that further cleanup is not practicable. If cleanup has not been attempted at all or there is a reliance on monitored natural attenuation (as in the case example), it may be difficult to provide direct evidence that cleanup is not practicable.

Has most of the contamination source been removed? If the great bulk of the contamination source has been removed and the remaining material constitutes only a small percentage of the original, then this may indicate the following.

(a) The groundwater contamination and its risk will diminish correspondingly, and the risk will not be unacceptable. In the case example, it is likely that the cleanup will have removed the bulk of the material, as the quantity of tar within the rock fractures may be relatively small. If no further cleanup is carried out, then monitoring may show that the risk will diminish over time as the contamination equilibrates with the relatively small amount of residual tar, and assist in achieving an acceptable risk situation.

(b) The cost of cleanup of the remaining contamination is much higher on a cost/unit quantity of contamination source than the initial cleanup, and there may be no net environmental benefit. The case example illustrates this, where cleanup of the residual tar in the rock is likely to require excavation of large quantities of rock, much of which is not contaminated. Environmental costs counterbalancing the benefits may be: energy and materials required for cleanup; lost landfill space and clean backfill; dust, noise and vibration associated with cleanup; resultant excavation may pose a water collection point and give rise to water logging and associated metals toxicity; and delays in site redevelopment.

Is treatment/removal of the remaining material technically feasible? Treatment of material located within rock fractures (particularly materials of high viscosity and/or high boiling points, such as tar) may not be technically feasible, and simple excavation may be the only technically feasible method of dealing with this type of material. It is unusual that simple excavation would not be technically feasible, although the cost may be very high. For example, excavation of rock is technically feasible (e.g. through use of excavator fitted with a rock breaker), and excavation underwater can be feasible. However, the concept of technical feasibility may not be in line with that of technical practicability. The USEPA has introduced the concept of 'technical impracticability' for groundwater contaminated sites, where

complete cleanup of the groundwater at certain sites is deemed to be impracticable due to complex technical and site-specific reasons (see, for example, *Guidance for Evaluating the Technical Impracticability of Ground-Water Restoration* - USEPA 1993).

Is treatment/removal of the remaining material financially viable? When the depth of contamination is out of reach of an excavator, or engineering major works are required to enable the cleanup (such as shoring unstable soil, dewatering, the nature of the material is intractable such as rock, the affected area is extensive, the site is confined by sensitive use activities, or landfill availability is limited), then the cost of removal of the contaminated material can be substantial and may be judged to be prohibitive. The cost may be beyond the financial capacity of the site owner to pay. Particularly for situations where there no net environmental benefit associated with this extensive cleanup, evaluating the financial costs related to cleanup can be an important factor in determining the overall site cleanup viability.

Does the groundwater contamination or its source adversely affect existing/likely/possible land use either on site or off site? Where volatile substances are present or the contamination is close to the surface, the contamination may adversely affect the use of the land by impacting human health or plant growth. This may be the situation in the case example, with volatile hydrocarbons such as benzene and toluene present in the tar. A formal risk assessment may be necessary to determine whether these volatile compounds pose a potentially unacceptable risk. If it is concluded that the contamination does not pose an unacceptable risk, this can be an important factor in accepting residual contamination. If, however, it is concluded that the contamination will adversely affect certain beneficial uses of the land, then there are a number of possible implications.

(a) If the effects are limited to *on site*, then it may be possible to avoid the adverse effect by restricting the use of the land, for example through a Statement of Environmental Audit and appropriate planning controls. For example, land use may be restricted to parkland (which may avoid problems with volatile substances), or to industrial or commercial use (which may avoid the need to sustain plant growth).

(b) If the effects also occur *off site,* restrictions on land use may not be an available option, unless the planning restrictions are such that land use is restricted in the long term (for example plant growth may not need to be sustained in a clearly commercial area such as in a central business district). The regulatory agencies generally seek to protect all possible land uses, although in evaluating whether cleanup is practicable the greatest priority will be afforded to existing and currently permitted land uses, and less priority will be afforded land uses which are not permitted under current zoning or are clearly very unlikely.

Does the contamination adversely affect existing/likely/possible groundwater use at the site or off site? The range of uses of groundwater that are possible will depend on the salinity of the groundwater, and may also depend on other factors such as yield. The relationship between salinity and use is defined in the groundwater policies that apply in the various states; the dependence on other factors is less well defined, and in most cases salinity is the determining factor. Where the salinity permits potable use, this will be often the limiting consideration, although other non-consumptive groundwater use scenarios include irrigation (watering of lawns and gardens) and swimming pool filling with subsequent exposure by pool users, which can also have stringent requirements. Discharge to surface waters can also be limiting in some situations, and is discussed in the following sections. Effects can be determined by comparing concentrations with guideline values, or exposure scenarios can be developed based on the likely frequency and magnitude of potential exposure.

(a) If the effects are limited to *on site*, then it may be possible to avoid the adverse effect by restricting the use of groundwater at the site. This is possible where the owner of the site understands and agrees to the limitation.

(b) If the effects also occur *off site*, limitations on use may not be possible, as it can be an 'as of right' use. It may be possible to limit use through a declaration that the groundwater is contaminated and not fit for use (such as through the Victorian "polluted groundwater zone"). Generally the regulatory agencies assign a high priority to avoiding off-site contamination where possible, and the requirements to achieve practicable cleanup can be expected to increase in cases where the source of contamination is on site and affects off-site groundwater usage. The highest priority will be to remove or reduce on-site *sources* so that off-site effects are avoided and likely or possible uses are enabled. Where cleanup has removed the source, then the priority for cleanup of the remaining dissolved-phase contamination will depend on the likelihood of use (e.g. priority existing use downgradient > existing use in the region but not down gradient > likely or possible use in the region >unlikely but possible on the basis of salinity). For example, a low priority may be assigned to protecting groundwater for stock use in the central business district). Because the priorities are determined by the relevant regulatory agency, it is essential to determine the local jurisdictional requirements (e.g., the Victorian State Environment Protection Policy for groundwater).

WHEN IS THE RISK ASSOCIATED WITH DISCHARGES OF GROUNDWATER SIGNIFICANT?

It is a common situation where a contaminated groundwater zone discharges into a local surface water body (such as a river or estuary), and the concentrations of certain contaminants exceed the guideline values for protection of aquatic ecosystems at the point of discharge. While the exceedances may be of concern, by themselves they do not necessarily indicate that 'harm' to ecological receptors in the river is in fact occurring. Rather, the exceedances should be considered to be a trigger that indicates that a more detailed study is needed.

> Example for consideration: Gasworks site where the groundwater is contaminated by polycyclic aromatic hydrocarbons (PAHs), benzene and other monoaromatic hydrocarbons, and ammonia; the site is located on a river; the site and river bank comprises reclaimed land; sediments in the river are partially dredged; the contaminated groundwater discharges to the river; and the concentrations of contaminants in the groundwater at the point of discharge (before dilution) exceed the guidelines for protection of aquatic ecosystems; some localised sources of groundwater contamination still remain on the site, but are ill-defined in location and extent and are judged to be impractical to cleanup.

In addressing this problem, regulatory policy will normally require protection of the aquatic ecosystems in the river, and this in turn will require the concentration of contaminants in the groundwater at the point of discharge (prior to dilution in the river water) to comply with the requirements for protection of aquatic ecosystems. Usually there will be no provision for relaxation of the requirements on the basis of the modified nature of the river ecosystems

in the vicinity of the discharge, or the geographical extent of the discharge (i.e. whether highly localised or extensive).

Nevertheless, in NSW environmental legislation introduces the concept of 'significant risk of harm' (and if the risk is not judged to be significant then cleanup can proceed without reference to the EPA), and in Victoria regulatory policy allows the Authority to accept contamination where there is 'no unacceptable risk'. 'Significant risk of harm' is a concept taken from the *Contaminated Land Management Act 1997*, and in NSW refers to sites *'where the contamination is considered to be serious and requires EPA regulatory intervention.'* (NSW EPA 1999). The NSW EPA has defined 'harm' to mean *'harm to human health or some aspect of the environment ... including any direct or indirect alteration of the environment that has the effect of degrading the environment whether in, on or under the land or elsewhere.'* (NSW EPA 1999). Auditors are faced with making decisions as to whether the risks associated with a contaminated site are acceptable or unacceptable. Current regulatory guidance does not provide a clear basis for decision making on these points, as 'acceptable' and 'unacceptable' risks have not been defined except in qualitative terms.

Several concepts need to be introduced in evaluating the potential impacts associated with this situation. The first is the concept of the mixing or attenuation zone, which is typically applied to effluent discharge locations where the designated environmental values are not protected (ANZECC 1999). The second concept is a fundamental concept in ecological risk assessment, wherein the level of protection to be provided is at the *population* level (as compared to human health risk assessment, where protection is provided to the individual). Both of these concepts have relevance when considering discharge of contaminated groundwater into a river environment.

In order to provide a framework for decision making, the following questions are proposed for consideration.

Are aquatic ecosystem criteria exceeded at the point relevant to aquatic ecosystems? An initial assessment of potential risk is usually made by comparing measured concentrations with published aquatic protection criteria. The National Environmental Protection Measure (NEPM 1999) provides a framework for the application of the Australian Water Quality Guidelines and relevant criteria for fresh and marine waters. While the NEPM provides groundwater investigation levels designed to protect aquatic ecosystems, it also allows for site-specific risk assessment. The NEPM recommends an iterative approach to site investigation and risk assessment, to provide for, as necessary, site-specific approaches to the assessment and management of potential risks. Thus a site-specific risk assessment is often needed to confirm whether criteria exceedances are actually posing a risk to the aquatic ecosystem.

What environmental values need to be protected at the point of groundwater discharge? Ecological values need to be defined for each site, since they will be used to determine the level of ecological protection to be provided. The draft National Framework for Ecological Risk Assessment of Contaminated Sites (Environment Australia 1997) notes that there are three primary considerations in the identification of ecological values for a site. These include societal relevance, ecological significance, and economic significance. In the guidelines it is noted that state environmental regulatory agencies, in consultation with ecological experts, industry, and the local community are expected to determine the relevant ecological values for a site. These values could, for example, be limited to the passage of fish in some locations, while allowing for spawning and breeding activities in other locations. The water quality standards consistent with protecting these ecological values would vary, with greater protection provided to spawning and breeding than to passage of fish.

Is it appropriate to allow a mixing zone where contaminants may exceed local ecosystem protection guideline values? Mixing zones may be an acceptable part of an overall site management program for certain sites. The mixing zone concept, which has been well accepted for point source discharges (e.g., storm drains, industrial outfalls, sewage treatment plant outfalls), has not traditionally been applied to discharges from contaminated sites. However, some of the concepts have merit for difficult sites and should be considered. The NEPM notes that some jurisdictions allow for a mixing zone while others apply the groundwater investigation levels (GILs) at the point of discharge without mixing in order to protect benthic organisms. The draft ANZECC/ARMCANZ fresh and marine water quality guidelines (ANZECC and ARMCANZ 1999) discuss mixing zones in relation to effluent outfalls. In discussing management of mixing zones, the ANZECC/ARMCANZ guidelines note that mixing zones are typically only acceptable when alternative means of effluent disposal are not best practice, when human exposures do not occur, and in settings where the discharge can be managed (e.g., shut off or modified). For many environmental sites, alternate solutions (groundwater extraction and treatment, barrier walls, etc.) exist and so discharge of contamination can be avoided. But for certain sites (such as in the case example), an idealised remedial solution is not possible and discharge will occur. For these sites the concept of a mixing zone should be considered valid.

If a mixing zone is allowed, then it must then be determined what types of impacts are considered acceptable in the mixing zone. ANZECC/ARMCANZ makes several recommendations for the management of mixing zones:

(a) toxicity testing of effluent should be considered;
(b) release may only be permitted under specified hydrological conditions, such as river flow rates (which may require the river flow to be large compared with the groundwater flow, and there not to be a seasonal low flow);
(c) the areal extent of mixing zones should be restricted so that the overall integrity of the ecosystem is not compromised (e.g., the entire width of the stream is not occluded so that migrating species can avoid the contaminated zone);
(d) release of effluent may need to be pulsed to maximise the possibility of ecological recovery between episodes if the discharge is significant with respect to the overall river flow (pulsed flow would be difficult to manage with respect to groundwater, should this be required); and
(e) monitoring programs may be mandatory (biological as well as hydrological).

Is the effect on aquatic ecosystems significant in terms of ecosystem populations? A fundamental tenet of ecological risk assessment is that the level of protection to be provided is at the *population* level (except in the case of endangered species, where protection of individual organisms may be provided). This may be compared to human health risk assessment, where protection is provided to the individual. Inherent in the concept of population protection is the fact that not every organism can be protected. Ecological risk assessment aims to provide protection at the population level, to ensure that the reproduction and development of a population of organisms within the wider ecosystem is not impacted. From a practical standpoint, this means that localised impacts may be acceptable as long as the reproductive success of an organism is not diminished within their entire ecosystem. An obviously important issue is defining localised impacts, as there are no clear guidelines that can be referenced. However, as long as the contamination does not affect the viability of the overall population(s), it may be argued that the impact is localised and from that standpoint, acceptable and not significant.

The specific toxic effects of the groundwater contaminants must be considered as part of any ecological risk assessment activity. Chemicals that have adverse reproductive or

development effects are typically of greatest concern to ecological receptors, since they can affect the viability of a population. Bioaccumulative chemicals are also of concern, since even low levels of them can build up in the food chain. Impacts to the most sensitive species is typically considered relevant, since removal of a single species can have a significant effect on the overall food chain.

In evaluating the potential ecological impacts associated with groundwater contamination, it is important to consider exposure to organisms that may be exposed directly at the groundwater:surface water interface. The interface commonly referred to is the pore water to which bottom dwelling organisms (benthic organisms) will be exposed as groundwater seeps into the stream or river. These organisms will have a higher relative exposure to groundwater contaminants than will organisms in the water column. However, the exposures will be limited to only those areas where the groundwater seepage is occurring. The seepage area, while it may extend the entire length of a site, may be quite small in relation to the overall habitat of the population of organisms.

Impacts to the benthic organisms can be evaluated through the use of such tests as the Rapid Bioassessment Protocol (RBP), which compares the density and diversity of species between the test area and a reference station. The extent of potential impact, and the acceptability of any impact, has to be established on a site-by-site basis. However, because benthic organisms may be exposed to contaminant concentrations in the undiluted groundwater, the potential impacts to these organisms may be greater than to those living in the water column.

CONCLUSIONS

Determining whether cleanup has been carried out to the extent practicable, and whether the risk posed by the residual contamination is acceptable is challenging from a technical, legal and regulatory viewpoint. Decision making requires consideration of a number of site-specific issues, some of which are outlined in this paper. While risk assessment is a key component of the decision making, it is important that the findings of the site assessment and risk assessment be interpreted in the context of relevant regulations. A risk-based approach that is part of an overall site management plan provides a solid framework for supporting and defending the selected approach.

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A Physically Representative, Analytically Based, Screening Tool for Unsaturated Solute Migration

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ABSTRACT: This paper presents a relatively simple approximate approach, based on a solution to the advection-dispersion equation, for predicting solute migration through the unsaturated zone under climatic influences. The solution considers the soil profile to be composed of two layers: the first to represent root zone conditions; the second for the sub-root zone. The main approximation with the procedure is the use of a constant coefficient form of the transport equation. The validity of this is established by showing that advective transport, in a spatially transformed equation, is determined by the cumulative infiltration and transpiration. In a key part of this approach, the vertical water content profile is explained using a quasi-steady state approximation that allows for layering in the soil profile and root water uptake. A physical justification for this approach is that water movement inputs and outputs are smoothed by the soil profile, such that at depth the water profile is a result of the average surface conditions. Results from the developed procedure compare well with numerical analyses using the SWIMv2 model with dynamic surface conditions.

KEYWORDS: solute transport, analytical models, screening tools

INTRODUCTION

The vertical migration of a dissolved solute through the unsaturated zone is a problem of broad practical importance. The advection-dispersion equation is a popular starting point for predictive analyses of the transport process and a wide range of solutions to this are in the literature. Robust numerically based solutions are available, suitable for a wide range of physical problems (i.e. Wagenet and Hutson 1986, Leonard *et al.* 1987). However there is a demand for solutions that, while perhaps being less accurate, offer compromises in terms of computational overheads and parameter requirements. One example is as conservative screening tools where analytical solutions have found increasing application (i.e. Beltman *et al.* 1995, Whelan *et al.* 2000).

In order for the mathematical problem to be tractable analytically, existing solutions involve a number of approximations about the manner in which the physical system is represented. One common approximation is to assume the advection-dispersion equation has constant coefficients (Elrick *et al.* 1994, Sun *et al.* 1999). For transport in the unsaturated zone this means that retardation, degradation and dispersion are constant throughout the unsaturated profile. Many soils exhibit a biologically active zone, roughly corresponding to the root zone, where the organic content and oxygen concentration are higher than deeper in the profile (Jury and Gruber 1989). For many contaminants this biologically active zone will mean that degradation and retardation rates are higher than deeper in the profile. In addition to vertical differences in transport properties, there can be a contrast in soil hydraulic properties. Also, the uptake of water by plants can act to concentrate solutes. Bosma and van der Zee

(1992) derived an analytical solution using a travelling wave approximation to simplify the advection-dispersion equation for solute transport in layered soils.

Another important approximation is in how water movement is represented in analytical solutions. The advection-dispersion equation is coupled to water movement and accurate solutions involve simultaneous numerical solution of Richard's equation for water movement (ie. SWIM model of Verburg *et al.* (1996)). With analytical solutions the description of water movement is considerably simplified to facilitate deriving the solution. These simplifications can consist of at least steady-state water movement (i.e. Elrick *et al.* (1994) who used Gardiner's steady state equation), or vertically uniform water content (i.e. Bosma and van der Zee 1992). The impact of these water movement and transport property assumptions has yet to be adequately investigated but will depend on the nature of the flow and transport problem being considered.

This paper presents the derivation of a two-layer quasi-analytical solution to vertical solute transport and a physical justification for the use of quasi-steady state water movement with analytical solutions for solute transport. In addition, a novel multi-layer procedure for quasi-steady state water movement with plant water use is presented. The two-layer advection-dispersion solution is combined with the quasi-steady state water movement relation to provide an approximate method for modelling solute transport. This approach is tested against a hypothetical simulation using the SWIMv2 model.

MATHEMATICAL DERIVATION

Introduction

The unsaturated advection-dispersion equation is derived by combining the solute mass flux with conservation of mass, leading to,

$$\frac{\partial(c\theta)}{\partial t}+\rho\frac{\partial m_s}{\partial t}=\frac{\partial}{\partial z}\left[\theta D\frac{\partial c}{\partial z}\right]-\frac{\partial(qc)}{\partial z}+\mu\theta c \tag{1}$$

where c is the dissolved solute concentration, m_s the adsorbed mass, θ is volumetric water content, μ the degradation rate, ρ is the soil bulk density, D is the dispersion coefficient and q the water flux.

With a linear adsorption isotherm ($m_s = K_d$ c) and continuity of water mass, Eqn (1) becomes,

$$K_a\frac{\partial c}{\partial t}=\frac{\partial}{\partial z}\left[\theta D\frac{\partial c}{\partial z}\right]-q(z,t)\frac{\partial c}{\partial z}+(\mu\theta-S_w)c \tag{2}$$

where $K_a = \theta + K_d\rho$, and S_w is the sink/source of water.

In an extension of the approach of Barry and Sposito (1989), a more tractable form of the unsaturated transport equation can be derived using the following variable,

$$Q=\int_0^z K_a\, d\bar{z} \tag{3}$$

to transform Eqn (2) leading to

$$\frac{\partial f}{\partial t}=\frac{\partial}{\partial Q}\left[K_a\theta D\frac{\partial f}{\partial Q}\right]-\left[q(0,t)+\int_0^z S_w\, d\bar{z}\right]\frac{\partial f}{\partial Q}+\frac{(\mu\theta-S_w)}{K_a}f \tag{4}$$

where c(z, t) = f(Q,t).

Without plant water uptake Eqn (4) becomes,

$$\frac{\partial f}{\partial t}=\frac{\partial}{\partial Q}\left[K_a\theta D\frac{\partial f}{\partial Q}\right]-q(0,t)\frac{\partial f}{\partial Q}+\frac{\mu\theta}{K_a}f \tag{5}$$

TWO-LAYER QUASI-ANALYTICAL SOLUTION

Physical Basis

The bases for this analysis are the transformed Eqns, (4), for within the root zone, and (5), below the root zone. In a similar manner to other analytical approaches, the constant coefficient form of these equations is used. This means that the following terms are approximated by constants; $q(0,t)$, $K_a\theta D$, $\int_0^z S_w(\bar{z},t)d\bar{z}$, $\mu\theta/K_a$, and $S_w(z,t)$.

For many soil profiles it may be a reasonable approximation to assume that there is a compact root zone with more or less uniform root distribution, and thus vertically uniform plant water uptake, S_w. Therefore for the first of the two layers in our model, S_w could be approximated by a spatial constant within the layer. For the second layer, below the root zone, S_w is zero. For the first layer $\int_0^z S_w(t)d\bar{z}$ can be integrated to $S_w(t)z$. Replacing z by a constant, z_{av}, would mean that advective transport is overestimated above z_{av} and underestimated below that point, since $S_w(t)z$ acts to reduce the advective water flux in Eqn (4).

In an extension of the transform used by Barry and Sposito (1989), $Q' = Q - \int_0^t q(0,\bar{t})+S_w(\bar{t})z_{av}d\bar{t}$, can be substituted into Eqn (6), leading to,

$$\frac{\partial f'}{\partial t}=\frac{\partial}{\partial Q'}\left[K_a\theta D\frac{\partial f'}{\partial Q'}\right]+\frac{\mu\theta}{K_a}f' \tag{6}$$

This transformation removes the advective term from Eqn (4) and redefines the problem in a moving boundary form. While Eqn (6) does not form the basis of the analysis presented in this paper it does demonstrate that the advective component of transport, at a given time, is determined by the cumulative or net surface water flux up to that time, $\int_0^t q(0,\bar{t})d\bar{t}$ and the cumulative transpiration, $\int_0^t S_w(\bar{t})d\bar{t}$. To find the concentration at a time, q_0t and $S_{wa}t$ can replace the integral terms in the previous sentence, where q_0 and S_{wa} are averages. Setting aside water content effects, solute transport could then be modelled using readily available information on the surface water fluxes rather than simultaneous solution of the water movement equation.

However, while the advective component of transport can largely be described using averages of the surface water flux and root water uptake, in order to map a location to the Q transform space the water content profile is required. In addition, the modified dispersion and degradation terms in Eqn (4) involve the water content. In the constant coefficient approximation, representative values would need to be resolved for each layer.

Solution Derivation

The quasi-analytical solution involves division of the soil profile into two layers. Within each layer a constant coefficient form of the differential equations is solved analytically in Laplace space. These layer analytical solutions are then coupled together to provide a description for the dependent variable in Laplace space over the problem domain. Numerical Laplace inversion is then used to calculate values for the dependent variable at locations in time.

A generalised form of the transformed constant coefficient approximation for Eqns (4) and (5) is presented below,

$$\frac{\partial f_i}{\partial t} = \alpha_i \frac{\partial^2 f_i}{\partial {Q_i}^2} - \beta_i \frac{\partial f_i}{\partial Q_i} + \gamma_i f_i \tag{7}$$

where i refers to the layer number and $\alpha_i = K_{ai} <\theta D>_i$, $\beta_i = (q_{oi} + S_{wai} z_{avi})$, $\gamma_i = (\mu_i <\theta_i> - S_{wai})/K_{ai}$, and where S_{wa2} is zero. In Eqn (7) Q_i is defined as being local to each layer; i.e. $Q_i = \int_{z_{di}}^{z} K_{ai} d\overline{z}$, where z_{di} is the depth of the interface between the two layers.

Taking the Laplace transform of (7) leads to the following equation,

$$s\bar{f}_i - f_{oi} = \alpha_i \frac{d^2 \bar{f}_i}{d{Q_i}^2} - \beta_i \frac{d\bar{f}_i}{dQ_i} + \gamma_i \bar{f}_i \tag{8}$$

where f_{oi} refers to the initial value of f, in this case a constant. The analytical solution to (8) is of the following form,

$$\bar{f}_i = a_{i1} e^{b_{i1} Q_i} + a_{i2} e^{b_{i2} Q_i} + a_{i3} \tag{9}$$

where i refers to the layer to which the solution is applied.

Substituting (9) into (8) leads to the following,

$$b_{i,1} = \frac{\beta_i - \sqrt{\beta_i^2 + 4\alpha_i (s - \gamma_i)}}{2\alpha_i} \quad \text{and} \quad b_{i,2} = \frac{\beta_i + \sqrt{\beta_i^2 + 4\alpha_i (s - \gamma_i)}}{2\alpha_i} \quad \text{and } a_{i3} = f_{io}/(s - \gamma_i) \tag{10}$$

The coefficients a_{i1} and a_{i2} are determined from coupling the equations for each layer (defined by (9)) together and introducing the boundary conditions.

Known surface concentration; c(0,t) = $c_s(t)$ or in Laplace and transform space, $\bar{f}(Q_1 = 0) = \bar{c}_s(s)$.

With the above condition and using Eqn (9) defined for the first layer,

$$a_{11} = \bar{c}_s - a_{12} - a_{13} \tag{11}$$

For the lower boundary condition; c(L, t) = $c_L(t)$ which leads to,

$$a_{21} = \left[\bar{c}_L - a_{23} - a_{22} e^{b_{22} \Delta Q_2}\right] / e^{b_{21} \Delta Q_2} \tag{12}$$

In order to solve the dependent variable variation throughout the problem domain the two layer equations need to be linked together. The conditions applied to link the equations are continuity of mass and dependent variable.

Continuity of dependent variable is expressed as $\bar{f}_1(Q_1 = \Delta Q_1) = \bar{f}_2(Q_2 = 0)$, and with (9), (11) and (12), this leads to,

$$a_{12}\left[e^{b_{12}\Delta Q_1} - e^{b_{11}\Delta Q_1}\right] + a_{22}\left[e^{(b_{22} - b_{21})\Delta Q_2} - 1\right] = \left[\bar{c}_L - a_{23}\right] e^{-b_{21}\Delta Q_2} - \left[\bar{c}_s - a_{13}\right] e^{b_{11}\Delta Q_1} + a_{23} - a_{13} \tag{13}$$

where ΔQ_1 and ΔQ_2 are the depths in Q transform space of the first and second layers.

Continuity of solute mass in Laplace transform space can be written as,

$\bar{q}_{c1}(Q_1 = \Delta Q_1) = \bar{q}_{c2}(Q_2 = 0)$ in Q space,

$$\left[-[K_a\theta D]\frac{d\bar{f}_1}{dQ_1} + q\bar{f}_1\right]_{Q_1=\Delta Q_1} = \left[-[K_a\theta D]\frac{d\bar{f}_2}{dQ_2} + q\bar{f}_2\right]_{Q_2=0} \tag{14}$$

Substitution of (9), (11) and (12) and noting that $(q\bar{f}_1)_{Q_1=\Delta Q_1} = (q\bar{f}_2)_{Q_2=0}$ leads to,

$$\begin{aligned} &a_{12}[K_a\theta D]_1\left[b_{11}e^{b_{11}\Delta Q_1} - b_{12}e^{b_{12}\Delta Q_1}\right] + a_{22}[K_a\theta D]_2\left[b_{22} - b_{21}e^{(b_{22}-b_{21})\Delta Q_2}\right] \\ &\quad = \left[a_{23} - \bar{c}_L\right][K_a\theta D]_2 b_{21}e^{-b_{21}\Delta Q_2} + \left[\bar{c}_s - a_{13}\right][K_a\theta D]_1 b_{11}e^{b_{11}\Delta Q_1} \end{aligned} \tag{15}$$

Eqns (13) and (15) can be solved for the two unknowns, a_{12} and a_{22} that can then be used to find a_{11} and a_{21} using Eqns (11) and (12).

In order to find the value of the dependent variable at a location, numerical Laplace inversion is performed using the de Hoog algorithm (de Hoog *et al.* 1982). With this algorithm, the function, in this case Eqn (9), is evaluated at a number of locations in Laplace space and these values used to calculate the inverse. Since the coefficients of Eqn (9) are functions of the Laplace variable, s, these must be calculated at each inversion location.

Steady State Water Content Profile

At steady state, conservation of water mass within the root zone leads to,

$$K(h)\left[\frac{dh}{dz} - 1\right] = -S_w z - q_o \tag{16}$$

where h is the matric potential and K(h) is the unsaturated hydraulic conductivity. With $K(h) = K_s e^{\alpha_g h}$, Eqn (16) can be integrated to,

$$h = \frac{1}{\alpha_g}\ln\left[e^{\alpha_g(h_L+z-z_L)} + \frac{1}{K_s}\left(\frac{S_w}{\alpha_g} + S_w z + q_o - e^{\alpha_g(z-z_L)}\left[\frac{S_w}{\alpha_g} + S_w z_L + q_o\right]\right)\right] \tag{17}$$

where K_s is the saturated hydraulic conductivity, α_g is a hydraulic conductivity shape parameter, z_L is the depth of the layer and h_L the value of the matric potential at the layer base.

Eqn (17) relates matric potential to depth for a constant root water uptake. Layering (that can allow for vertical variation in hydraulic properties and root water uptake) can be incorporated by using Eqn (17) for each layer and solving upwards from the watertable, at which h_L =0, and equating h at the top of each layer with the overlying layer's h_L.

The water content profile is required in order to use the Q transformed transport equation presented above. The matric potential profile defined by Eqn (17) can be used with the moisture retention relationship, θ(h), to calculate the moisture content profile. The van Genuchten (1980) equation can be written as,

$$\frac{\theta - \theta_r}{\theta_s - \theta_r} = \frac{1}{\left[1 + \left(\frac{h}{h_g}\right)^n\right]^m} \tag{18}$$

where m=1-1/n, h_g is a scale parameter, n is a shape parameter, and θ_r is the residual water content.

TESTING OF TWO-LAYER SOLUTION

In this section the impact of transient water movement behaviour on the accuracy of the two-layer solution with steady state water movement will be investigated using a hypothetical simulation. The basis of comparison for this analysis is the SWIMv2 model of Verburg *et al.* (1996) that solves the coupled advection-dispersion and Richards' equations. In the SWIM simulation the van Genuchten moisture retention relationship was used with the Mualem hydraulic conductivity function. The soil hydraulic parameters used in this analysis came from van Genuchten (1980) for Guelph loam and are presented in Table 1. The α_g parameter, required for Eqn (17), was estimated by matching the values calculated with the exponential hydraulic conductivity to those from the Mualem function, with the van Genuchten parameter values, towards saturation.

Table 1. Soil hydraulic properties used in the model simulation

	θ_s ($cm^3\,cm^{-3}$)	θ_r ($cm^3\,cm^{-3}$)	K_s ($cm\,h^{-1}$)	h_g (cm)	m	α_g
Guelph loam	0.434	0.218	1.32	-50	0.275	0.12

Figure 1 presents the cumulative water infiltration and transpiration imposed in the SWIM simulations. Infiltration is composed of a series of discrete events of varying magnitude and time of separation. The rate at which transpiration occurs also varies but on a longer time frame. The simulations were for a vertical column of 10 m with vertically uniform hydraulic properties and a root zone of 20 cm. The initial water content profile for SWIMv2 was calculated using the steady state solution, Eqn (17), with the average of the infiltration and transpiration time series and 250 nodes.

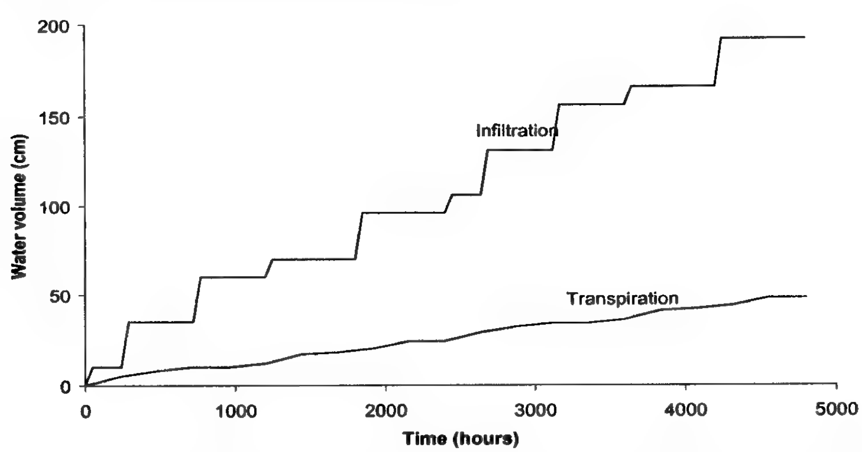

Fig. 1. The infiltration and transpiration (expressed as cumulative water volume) time series used in the simulation to test the two-layer solution for solute transport

Fig. 2 presents the solute concentration variation with time, for the two approaches, at a series of depths. Each two-layer result is calculated using the average of the infiltration and transpiration fluxes up to the time of interest. In general the results from the two procedures are in close agreement. Both sets of results show strong, infiltration event related, pulses of solute moving past the selected depths. The SWIM results show how these pulses become more dispersed the deeper they travel. The two-layer solution does not accurately represent this dispersion behaviour, a consequence of using the steady water assumption with average water fluxes. However the results from the two approaches converge rapidly following the arrival of each pulse.

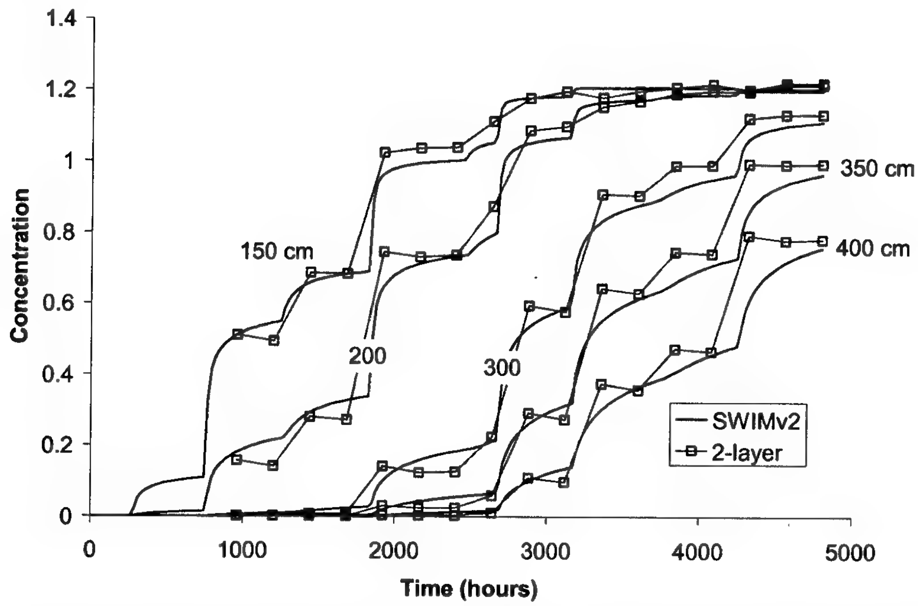

Fig. 2. Solute concentration variation with time at a number of depths calculated using SWIMv2 and with the two layer solution (average water flux varies between times) with Guelph loam hydraulic properties

CONCLUSIONS

This paper presents an approximate solution to unsaturated solute migration in soils subject to dynamic surface infiltration and transpiration. This approach is based on several simplifications; one of the most significant of these is in the representation of the transient water movement behaviour. Water movement was described as a quasi-steady state process using average infiltration and transpiration fluxes. However it was shown that, even for soils where there is a highly dynamic water movement, solute transport could be represented with a high degree of confidence. Even though the simulations used to test the methodology were hypothetical, they demonstrate the likely performance of the method for problems of unsaturated transport in field soils exposed to climate.

A key advantage of the approach presented in this paper is that it uses readily available information to represent water movement. Infiltrated volume, for many rainfall events and soils, is equivalent to the amount of rain. Actual transpiration can be estimated using a number of empirical formulas. Another advantage is that the event behaviour does not have to be resolved or the timing of events, but it is the cumulatives that are then converted to averages. This represents a significant simplification over the use of numerical solutions to coupled Richards' and advection-dispersion equations, where flux-based rainfall and transpiration are required. The infiltration and transpiration averages used in the two-layer

solution could also be used to calculate the steady solution providing a predictive approach to transport. However if the water content profile was known at key times of the year this information could be used directly to estimate the layer average water contents and to transform from Q to z space.

The method presented in this paper is approximate and cannot replace existing numerical solutions for problems where accuracy is required. However, because it is easy to apply it would be useful for calculations where more approximate information on solute migration is required. The two-layer solution would also allow greater investigation of the effects of parameter uncertainty since the method is quick and large numbers of realisations can be readily calculated. It could therefore be a useful approach for risk assessments of surface contamination. It would also allow procedures to be developed that are more physically based for vulnerability mapping.

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Flow and Transport Modelling for Back-calculation of Pre-emptive Groundwater Compliance Screening Levels: an Essential Component of Contaminated Sites Management (Aquatic Ecosystem Example)

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ABSTRACT: Australian regulators recognise the protection of aquatic ecosystems (PAE) as a groundwater beneficial use, based on the premise that groundwater and surface water systems may be hydraulically interconnected. PAE guidelines are based on groundwater concentrations *at the point of discharge to the ecosystem* (e.g. littoral zone), which necessarily is located some distance from the source site. Evaluation of potential PAE impact therefore requires assessment of various hydrogeological processes influencing the contaminant plume between the source and receptor. Monitored natural attenuation (MNA) strategies for contaminated site management place emphasis on *in situ* processes to achieve compliance (which may not occur), and therefore requires contingency options. An important contingency involves back-calculation of pre-emptive compliance (trigger) levels at wells located up gradient of the receptor, so that if compliance levels are exceeded active groundwater remediation is 'triggered' *at these points before impact to the receptor is allowed to occur.* A methodology for calculating pre-emptive compliance levels is presented, based on the Domenico (1987) analytical flow and transport model. A worked example is presented.

KEYWORDS: groundwater, natural attenuation, compliance levels, ecosystems

INTRODUCTION

The application of the monitored natural attenuation (MNA) strategy to the management of contaminated sites has recently undergone a dramatic increase, particularly in relation to groundwater contamination known to be susceptible to intrinsic biodegradation (e.g. petroleum hydrocarbons, chlorinated solvents). This situation has arisen from the recognition that traditional groundwater remediation methods (e.g. pump-and-treat, air sparging) have inherent limitations in meeting cleanup objectives within reasonable time frames, are capital-intensive and generally highly intrusive. MNA, when combined with source reduction activities and health and ecological risk assessment, may allow a site to be managed in a less intensive manner.

As MNA places emphasis, however, on natural attenuation to achieve compliance (which may or may not occur), appropriate application of the MNA strategy necessarily requires contingency options to be put in place. This is particularly the case where aquatic ecosystems are involved. The protection of aquatic (fresh or marine) ecosystems (PAE) is recognised as a special 'off-site' type of groundwater beneficial use under the 'Groundwaters of Victoria' SEPP (EPAV 1997), based on the premise that surface and groundwater systems are known to be hydraulically interconnected.

The PAE guidelines are based on groundwater concentrations *at the point of discharge to the ecosystem* (e.g. stream bank, littoral zone), which necessarily is located at some distance from the source site. Evaluation of potential PAE impact therefore requires assessment of

various hydrogeological processes (e.g. advection, dispersion, sorption, biodegradation) operating on contaminant plume mass and concentration between the source site and the PAE receptor. This can only be achieved by applying validated groundwater fate and transport models.

An essential contingency option where PAE guidelines are involved is the identification of pre-emptive compliance (or trigger) levels at pre-determined monitoring wells (or compliance wells) located in between the source site and the PAE receptor. If the adopted compliance levels are exceeded, this triggers immediate active groundwater remediation to reduce plume mass and/or concentration *at the point of compliance* (ie. pre-emptive remediation) *before exceedance at the point of discharge is allowed to occur.*

OBJECTIVES

Application of an MNA strategy is primarily based on a comprehensive groundwater monitoring and management plan (GMMP), which typically attempts to achieve the following objectives:

(a) demonstrate that natural attenuation and/or migration is occurring according to expectations (i.e. predictive modelling);
(b) determine if the plume is expanding (either downgradient, laterally or vertically), shrinking or remaining stable;
(c) serve as a compliance program, so that any impact to downgradient receptors is identified (relative to adopted trigger levels) before potential discharge occurs;
(d) detect new releases of contaminants to the environment that could impact on the effectiveness of the natural attenuation remedy;
(e) detect changes in environmental conditions (e.g.,hydrogeologic, geochemical or other changes) that may reduce the efficacy of any of the natural attenuation processes; and
(f) verify attainment of criteria or exceedance of trigger levels.

This paper focusses on the determination of trigger levels as required in part (c) of the GMMP. Such contingencies provide assurance that the remedy's protectiveness will be maintained should natural attenuation not progress as expected.

METHODOLOGY

The 'Groundwaters of Victoria' SEPP (EPAV 1997) provides the basis for the regulatory framework surrounding groundwater contamination issues in Victoria. The SEPP in turn is based on the concept of groundwater beneficial use(s), which are generally defined according to the total dissolved solids (TDS) content. Two special cases are the protection of both fresh and marine aquatic ecosystems (PAE), for which environmental guidelines are based on groundwater contaminant concentrations *at the point of discharge.* An essential component of the MNA-based GMMP is the setting of compliance (or trigger) levels for monitoring wells located between the source site and the potential receptor (e.g. private bore, estuary, coastline). The exceedance of compliance levels at selected compliance wells 'triggers' an immediate response in the form of more costly active, or engineered, groundwater remediation, in order to reduce concentrations below the compliance level before exceedance at the point of discharge occurs.

Evaluation of potential PAE impact therefore requires assessment of various hydrogeological processes (e.g. advection, dispersion, sorption, biodegradation) operating on

contaminant plume mass and concentration between the source site and the PAE receptor. This can only be achieved by applying validated groundwater fate and transport models. A methodology for setting pre-emptive compliance screening levels was developed by OTEK based on modification of the Domenico (1987) analytical flow and transport model. The Domenico model is widely recognised within industry and is the basis of the BIOSCREEN natural attenuation model (Newell *et al.* 1996). Although the model in its present form could be used to calculate trigger levels, this would require a time-consuming iterative approach, whereby numerous model runs and adjustments would be necessary before converging on the necessary PAE guideline concentration at the selected point of discharge. Recognising these limitations, OTEK modified the model to allow *back-calculation* of compliance concentrations at the point of discharge based on input of the following data:

(a) site-specific hydrogeological data (e.g. source dimension, advection, dispersion, sorption and biodegradation);
(b) the required PAE (or other) guideline concentration at the receptor;
(c) the distance of the compliance well from the receptor; and
(d) location of compliance point relative to the plume centreline.

The following sections describe the Domenico model and re-working to allow compliance level calculation.

DOMENICO ANALYTICAL MODEL

The Domenico model accounts for the effects of advective transport, three-dimensional dispersion, adsorption, and first-order decay, and assumes a fully-penetrating vertical plane source oriented perpendicular to groundwater flow, to simulate the release of organics to moving groundwater.

The Domenico model algorithm gives concentration as:

$$\frac{C(x,y,0,t)}{C_0} = \frac{1}{8}\exp\left[\frac{x}{2\alpha_x}\left(1-\left(\sqrt{1+\frac{4\lambda\alpha_x}{v}}\right)\right)\right] erfc\left[\frac{x-vt\sqrt{1+\frac{4\lambda\alpha_x}{v}}}{2\sqrt{\alpha_x vt}}\right]$$
$$\left(erf\left[\frac{y+Y/2}{2\sqrt{\alpha_y x}}\right]-erf\left[\frac{y-Y/2}{2\sqrt{\alpha_y x}}\right]\right)\left(erf\left[\frac{Z}{2\sqrt{\alpha_z x}}\right]-erf\left[\frac{-Z}{2\sqrt{\alpha_z x}}\right]\right)$$

where $$v = \frac{Ki}{\theta_e R}$$

and $C(x,y,z,t)$ = concentration at distance x downgradient of source and distance y from plume centreline at time t (mg L^{-1}); C_o = concentration is source zone at time $t = 0$ (mg L^{-1}); x = distance downgradient of source (m); y = distance from plume centreline of source (m); z = distance from surface to measurement point (assumed to be zero - concentration is always assumed to be at the top of watertable) (m); α_x = longitudinal groundwater dispersivity (m); α_y = transverse groundwater dispersivity (m); α_z = vertical groundwater dispersivity (m); θ_e = effective porosity; λ = first order degradation rate (day^{-1}); v = groundwater seepage velocity

(m $year^{-1}$); K = aquifer hydraulic conductivity (m $year^{-1}$); R = retardation factor; i = hydraulic gradient (m m^{-1}); Y = source width (m); Z = source depth (m).

The compliance (or trigger) level is equivalent to the source concentration parameter at time t=0 (C_0). If $C(x,y,z,t)$ is known, then substitution of these parameters into the Domenico model will give C_0.

The desired C (x,y,z,t) (equivalent to the desired regulatory concentration at the point of discharge) is X mg L^{-1}. This is placed on the left hand side of the above equation, so that:

$X/C_0 = beta$ (=right hand side of Domenico model).

When *beta* is calculated for a pre-determined x, y and t, then C_0 may be calculated by dividing *beta* by X.

The distance x is equivalent to the distance between the compliance well (which in this case represents the source zone) and the receptor.

The distance y is set at zero, as the plume will migrate fastest along the plume centreline (i.e. y=0) and compliance levels should account for this worst-case situation. If, however, the compliance well is necessarily placed off-centre from the plume centreline, this can still be accounted for by calculating the perpendicular distance from the plume centreline to the compliance well.

The distance z is also set at zero for reasons already stated above. If however z is known (e.g. as indicated in multi-level monitoring wells), then this data can be used.

The time t is taken as the travel time from the compliance well to the receptor creek. This is pre-calculated using Darcy's Law and accounting for retardation, by the equation:

$t = x/(v)$, where v = retarded chemical velocity

Substituting all the above values into the Domenico equation, C_0 is solved. This re-worked Domenico solution is easily constructed using any spreadsheet software.

Model Assumptions

The key assumptions in the model are:

(a) the aquifer and flow field are homogenous and isotropic;
(b) the groundwater velocity is fast enough that molecular diffusion in the dispersion terms can be ignored; and
(c) adsorption is a reversible process represented by a linear isotherm.

Model Limitations

The model has some key limitations.

(a) The Domenico analytical model assumes simple groundwater flow conditions. The model should not be applied where pumping systems create a complicated flow field. In addition, the model should not be applied where vertical flow gradients affect contaminant transport.
(b) As an screening tool, the model only approximates more complicated processes that occur in the field.
(c) The Domenico model is not formulated to simulate the effects of chemical diffusion. Therefore, contaminant transport through very slow hydrogeologic regimes (e.g., clays and slurry walls) should probably not be modeled unless the effects of chemical diffusion are proven to be insignificant.

WORKED EXAMPLE

The application of the 'trigger level' model is best illustrated using a worked example, which in this case is based on a site located 200 m from the coastline. The site represents the source for a dissolved-phase benzene plume, which is in steady state and has migrated a maximum distance of 50 m off-site. Two compliance wells are located along the plume centreline at distances of 125 m and 50 m respectively from the coastline. The regulatory PAE guideline for benzene at the point of discharge is 0.3 mg L^{-1} (EPAV 1997). What are the benzene compliance levels at the two compliance wells which are protective of the 0.3 mg L^{-1} PAE guideline and which, if exceeded, require the implementation of active groundwater remediation?

Model Input Parameters

Hydraulic conductivity, gradient and effective porosity

The site aquifer lithology consists of silty sands. The hydraulic conductivity (*K*) and hydraulic gradient (a) at the site were measured at 1 m day^{-1} (or 0.005 cm s^{-1}) and 0.002 m m^{-1} respectively. The effective porosity was based on published literature values and assumed to be 0.15.

Soil Bulk Density and Sorption

The bulk density was set at 1.7 Mg m^{-3}, and fraction organic carbon (foc) at 0.001. The soil-organic carbon partition coefficient (KOC) for benzene is assumed to be 83 L kg^{-1} (ASTM 1995). This gives a distribution coefficient of 0.083 Lkg^{-1}.

First-order decay rate

The Domenico model assumes that the solute degradation rate is proportional to the solute concentration. The higher the concentration, the higher the degradation rate. This is a conventional method for simulating biodegradation in dissolved hydrocarbon plumes.

First-order decay rates or half lives for chemicals can generally be found in the published literature (e.g. Verscheuren 1983) or can be estimated using monitoring data and regression methods (Buscheck and Alcantar 1995). For the purposes of this case study, the first order decay rate is assumed at 0.01 day^{-1}.

Dispersivity

Dispersion refers to the process whereby a plume will spread out in a longitudinal direction (along the direction of groundwater flow), transversely (perpendicular to groundwater flow), and vertically downwards due to mechanical mixing in the aquifer and chemical diffusion. Selection of dispersivity values is a difficult process, given the impracticability of measuring dispersion in the field.

Longitudinal Dispersivity

The equation used for estimating longitudinal dispersivity is based on field data compiled by Gelhar *et al.* (1992), and which was statistically analysed by Xu and Eckstein (1995) to give the following expression for α_x as a function of plume length:

$$\alpha_x = 3.28.0.83.\left[\log_{10}\left(\frac{L_p}{3.28}\right)\right]^{2.414}$$

Transverse Dispersivity

Based on high reliability points, Gelhar *et al.* (1992) gives the following expression for transverse dispersivity as a ratio to longitudinal dispersivity:

$$\alpha_y = 0.1\alpha_x$$

Vertical Dispersivity

α_z is typically very low, and here is assumed to be 0.01 of α_y.

Source (or plume) width and depth

The source (or plume at distance from the source) width is typically derived from two-dimensional plume delineation maps. The source thickness is either calculated from multi-level monitoring well data or assumed. At distance from the source, most petroleum-based plumes may be assumed to be relatively thin (around 1 to 2 m). Larger values would be expected for solvent-based plumes. For this example, the plume width and thickness are assumed to be 20 m and 1 m respectively.

SPREADSHEET MODEL RESULTS

The above data was input to OTEK's spreadsheet model, and the results are presented graphically in Figs 1 and 2. The model calculates compliance levels of 1.9 and 1.0 mg L^{-1} at the farthest and closest compliance points respectively. These levels are then formally recognised in the GMMP and monitoring results are compared against these levels on an ongoing basis, until either compliance is achieved or the levels exceeded.

CONCLUSIONS

The re-worked Domenico model as presented above is considered to represent a valuable tool in the management of contaminated sites where off-site groundwater contamination is present. This is particularly the case for aquatic ecosystems located at some distance from a contaminated source site, where the introduction of pre-emptive groundwater trigger levels as a contingency option strengthens the principle of applying MNA as a management approach.

TRIGGER LEVEL CALCULATIONS

BACK CALCULATION FROM RECEPTOR TO COMPLIANCE WELLS

COPC: ***BENZENE***

DATA INPUT

Receptor			
Crec	0.30	mg/L	Desired Concentration at Receptor
x	410	feet	Receptor Distance from Compliance Well
y	0	feet	Distance from Centreline to Compliance Well
TTR	11.54	years	Travel Time to Receptor (years)
Source Dimension			
Sw	60	feet	Source Width
Sd	3	feet	Source Depth
Groundwater Flow			
K	5.0E-03	cm/sec	Hydraulic Conductivity
i	0.002	m/m	Hydraulic Gradient
ne	0.15	dimless.	Effective Porosity
Vur	69.0	feet/year	Average Linear Groundwater Velocity
Retardation			
BD	1.7	g/cc	Bulk Density
KOC	83	cc/g	Organic Carbon Coefficient
foc	0.001	g/cc	Fraction Organic Carbon
Kd	0.083	g/cc	Distribution Coefficient
R	1.94		Retardation Coefficient
Vc	35.6	feet/year	Retarded Contaminant Velocity
Dispersivity			
PL	410	feet	Plume Length (INPUT FOR CALC BELOW)
alpha (L)	16.3	feet	Longitudinal Dispersivity
alpha (T)	1.6	feet	Transverse Dispersivity
alpha (V)	0.016	feet	Vertical Dispersivity
Biodegradation Decay			
lamda	0.0100	1/day	biodegradation decay rate

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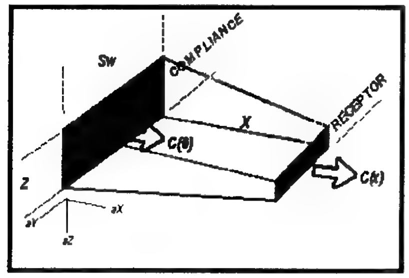
DOMENICO ANALYTICAL MODEL

$$\frac{C(x,y,0,t)}{C_0} = \frac{1}{8}\exp\left[\frac{x}{2\alpha_x}\left(1-\left(\sqrt{1+\frac{4\lambda\alpha_x}{v}}\right)\right)\right]erfc\left[\frac{x-vt\sqrt{1+\frac{4\lambda\alpha_x}{v}}}{2\sqrt{\alpha_x vt}}\right]$$

$$\left(erf\left[\frac{y+Y/2}{2\sqrt{\alpha_y x}}\right]-erf\left[\frac{y-Y/2}{2\sqrt{\alpha_y x}}\right]\right)\left(erf\left[\frac{Z}{2\sqrt{\alpha_z x}}\right]-erf\left[\frac{-Z}{2\sqrt{\alpha_z x}}\right]\right)$$

$$where: v = \frac{Ki}{\theta_e R}$$



TRIGGER LEVEL: 1.9 mg/L

Fig. 1. PAE Trigger Level for Compliance Well 125 m (410') from Receptor

TRIGGER LEVEL CALCULATIONS

BACK CALCULATION FROM RECEPTOR TO COMPLIANCE WELLS

COPC: ***BENZENE***

DATA INPUT

Receptor			
Crec	0.30	mg/L	Desired Concentration at Receptor
x	164	feet	Receptor Distance from Compliance Well
y	0	feet	Distance from Centreline to Compliance Well
TTR	4.62	years	Travel Time to Receptor (years)
Source Dimension			
Sw	60	feet	Source Width
Sd	3	feet	Source Depth
Groundwater Flow			
K	5.0E-03	cm/sec	Hydraulic Conductivity
i	0.002	m/m	Hydraulic Gradient
ne	0.15	dimless.	Effective Porosity
Vur	69.0	feet/year	Average Linear Groundwater Velocity
Retardation			
BD	1.7	g/cc	Bulk Density
KOC	83	cc/g	Organic Carbon Coefficient
foc	0.001	g/cc	Fraction Organic Carbon
Kd	0.083	g/cc	Distribution Coefficient
R	1.94		Retardation Coefficient
Vc	35.6	feet/year	Retarded Contaminant Velocity
Dispersivity			
PL	410	feet	Plume Length (INPUT FOR CALC BELOW)
alpha (L)	16.3	feet	Longitudinal Dispersivity
alpha (T)	1.6	feet	Transverse Dispersivity
alpha (V)	0.016	feet	Vertical Dispersivity
Biodegradation Decay			
lamda	0.0100	1/day	biodegradation decay rate

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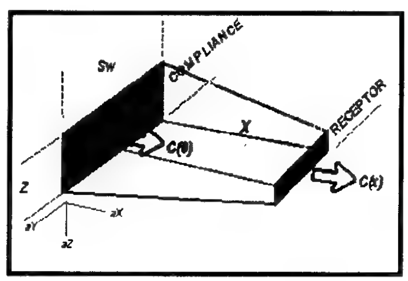
DOMENICO ANALYTICAL MODEL

$$\frac{C(x,y,0,t)}{C_0} = \frac{1}{8}\exp\left[\frac{x}{2\alpha_x}\left(1-\left(\sqrt{1+\frac{4\lambda\alpha_x}{v}}\right)\right)\right]erfc\left[\frac{x-vt\sqrt{1+\frac{4\lambda\alpha_x}{v}}}{2\sqrt{\alpha_x vt}}\right]$$

$$\left(erf\left[\frac{y+Y/2}{2\sqrt{\alpha_y x}}\right]-erf\left[\frac{y-Y/2}{2\sqrt{\alpha_y x}}\right]\right)\left(erf\left[\frac{Z}{2\sqrt{\alpha_z x}}\right]-erf\left[\frac{-Z}{2\sqrt{\alpha_z x}}\right]\right)$$

$$where: v = \frac{Ki}{\theta_e R}$$



TRIGGER LEVEL: 1.0 mg/L

Fig. 2. PAE Trigger Level for Compliance Well 50 m (164') from Receptor

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Initial Site Characterisation of a Dissolved Hydrocarbon Groundwater Plume Discharging to a Surface Water Environment

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ABSTRACT: Preliminary characterisation of a dissolved hydrocarbon groundwater plume flowing towards a tidally- and seasonally-forced estuarine system has been completed at a site in Perth, Western Australia. Installation and sampling of multiport boreholes enabled fine scale (0.5-m) vertical definition of hydrocarbon concentrations. Vertical electrical conductivity profiles from multiport and spear probe sampling into the river sediments indicated that two groundwater/river water interfaces or dispersion zones are present: (a) an upper dispersion zone between brackish river water and groundwater, and (b) a lower interface between groundwater and deeper saline water. On-line water level loggers show that near-shore groundwater levels are also strongly influence by tidal oscillation. Results from the initial site characterisation will be used to plan further investigations of contaminated groundwater/surface water interactions and the biodegradation processes occurring at the site.

KEYWORDS: petroleum hydrocarbons, groundwater, surface water, leaking underground storage tanks, characterisation.

INTRODUCTION

Interactions between groundwater contaminant plumes and surface water bodies, particularly in coastal and estuarine environments, are currently not understood well, although there have been some recent studies for freshwater environments (e.g., Lorah and Olsen 1999). Much urban and industrial infrastructure borders such environments. Sites where groundwater/surface water interactions occur present challenging remediation and monitoring problems. This paper details the initial site characterisation findings of an in-progress two-year field investigation of a dissolved petroleum hydrocarbon groundwater plume that discharges into the tidally- and seasonally-forced river estuarine system situated on the Swan Coastal Plain in Perth, Western Australia.

The estuary is characterised by cyclical density stratification due to a marine salt wedge migrating up the estuary during spring and summer. Regression of the salt wedge occurs during autumn and winter due to fresh water flushing of the estuary. The estuary also receives input from groundwater discharge along its margins that also varies seasonally. Recent studies (Smith and Turner 2000) show that the seasonal density contrasts between the estuary and adjacent fresh groundwater system are sufficient to drive mixed-convection cells beneath the estuary and recirculation of estuarine water in the aquifers. The fate and transport of contaminants dissolved in groundwater that interacts with such dynamic estuarine systems is understudied and poorly understood. The site described here provides an ideal opportunity to develop this understanding.

SITE DESCRIPTION

The study site is situated on the river foreshore (see Fig. 1) in metropolitan Perth, Western Australia. Groundwater at the site is impacted with dissolved-phase petroleum hydrocarbons, including the BTEX (benzene, toluene, ethylbenzene, and isomers of xylene) aromatic compounds. These impacts originate from unintentional LNAPL (light nonaqueous phase liquid) release from underground storage tanks (USTs). A dissolved hydrocarbon groundwater plume emanates from a historical source and follows an easterly flow path as governed by the local groundwater hydraulics. The source is located approximately 70 m from the river's edge.

The hydrogeology at the site is dominated by highly permeable alluvial sands of Quaternary age that form part of the wide spread unconfined 'superficial aquifer' of the Swan Coastal Plain (Davidson 1995). The sediments comprise well-sorted, medium-grained (effective grain size of 1 mm), well-rounded quartz and shell grains. The thickness of the superficial aquifer at the site is unknown. The Quaternary Tamala Limestone Formation is interpreted to underlie the superficial aquifer. Regionally the site is located at the edge of the Jandakot groundwater mound where it receives only 0-5% of rainfall recharge contributing to the groundwater flow (Davidson 1995). Dissolved oxygen and redox potential values indicate that the groundwater is anaerobic (i.e., under reducing conditions). Aquifer properties were estimated as 28-125 m year^{-1} for groundwater flow, 35-40% for the saturated porosity, and 5-20 m day^{-1} for the hydraulic conductivity (see, for example, Davidson 1995). The average hydraulic gradient from the source to the river foreshore is about 0.01.

Periodic monitoring at the site since 1993 showed an elongated hydrocarbon plume that may be impacting the river foreshore. Benzene concentrations on the river bank were deemed in excess of ANZECC guidelines (1992). The current study, initiated in January 2000, aims to map the plume in three dimensions, quantify hydrocarbon fluxes at the groundwater/river water interface including natural attenuation processes, and to monitor the behaviour of the plume over tidal and seasonal periods.

METHODS

The current work program involves mapping the three-dimensional dissolved hydrocarbon distribution in the subsurface around the groundwater/saline river water interface. Additionally, inorganic analyses and monitoring are planned to delineate redox zones and to evaluate the natural attenuation potential of the plume. Sampling and monitoring infrastructure installed at the site includes (see Fig. 1):

(a) Two permanent multiport boreholes (C-MP01 and C-MP02) installed to depths of 8 m below ground level with 0.1-m long screens at 0.5-m depth intervals. The multiports boreholes were constructed by initially auguring to the water table using a half split stem auger followed by insertion of casing into the hole and then sludging aquifer material until the required depth was reached. The multiport bundle was then installed through the casing, which was removed to allow the hole to collapse around the installation. Each multiport borehole consisted of a bundle of 2.5-mm internal diameter nylon tubes, with 0.1-m slotted stainless steel tube screens covered by an inert nylon filter mesh.

(b) Four on-line water level loggers. One logger was placed in the river to monitor river water levels, and the other three were located at 8 m (MW33), 18 m (MW42) and 50 m (MW18) from the shoreline, in order to monitor groundwater levels progressively away from the river shoreline along the proximal path of the contaminant plume.

The multiports were initially sampled on two separate occasions to determine the vertical concentration profile of the contaminant plume. Both multiport boreholes were sampled over a part tidal period to gauge tidal variability in groundwater quality parameters. The 4.5-m deep sampling port at C-MP02 was sampled hourly over the tidal period for hydrocarbon contamination. Groundwater samples were recovered via suction directly from the access lines of the multiport boreholes using glass syringes after purging of the lines. This strategy was adopted to minimise disturbance of the groundwater and sorptive and/or volatile losses of the volatile BTEX compounds (Davis *et al.* 1999).

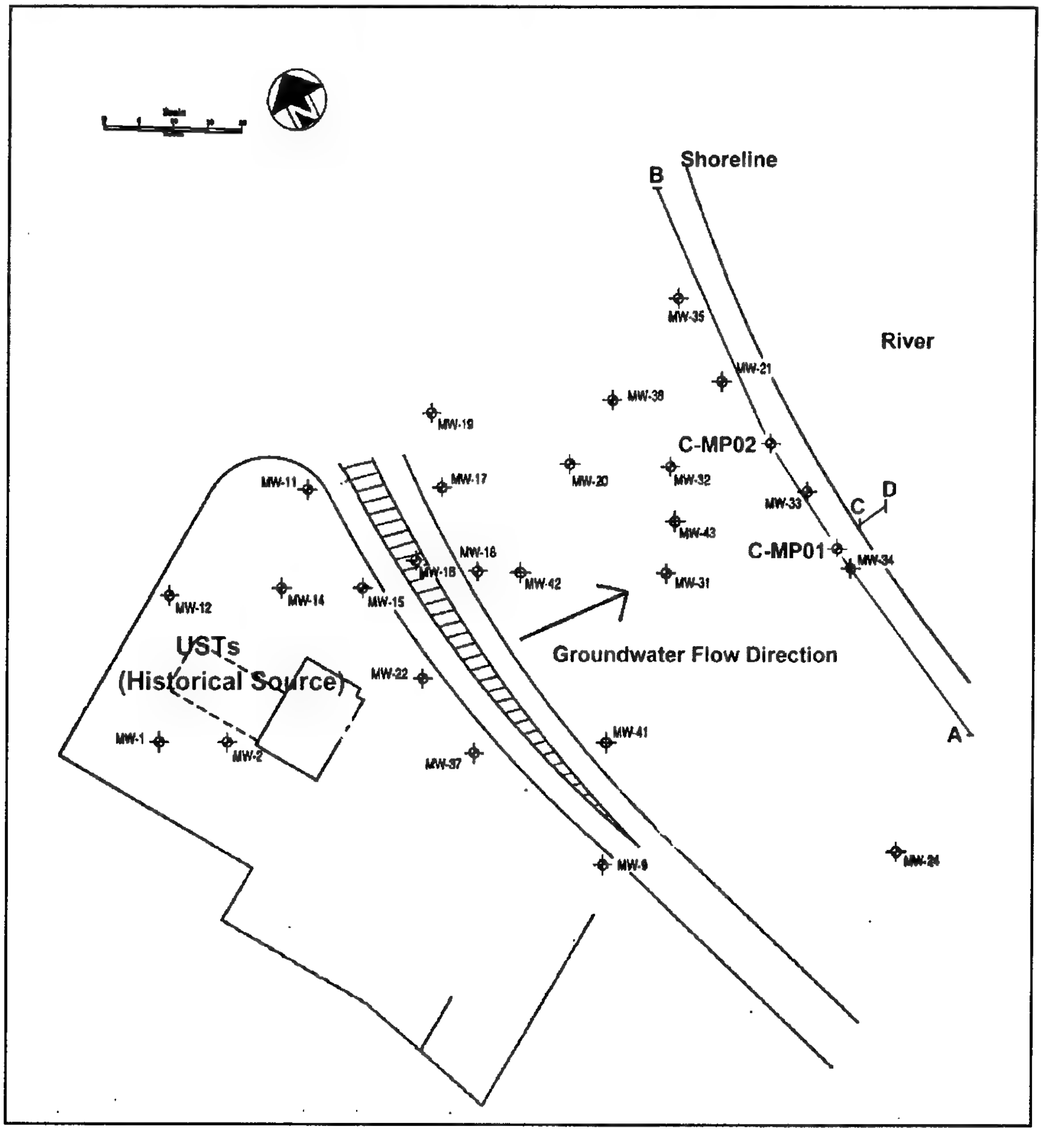

Fig. 1. Site map showing the location of monitoring wells, multiport boreholes and sampling transects

In order to delineate the lateral extent of the plume along the river foreshore and into the river, reconnaissance-style spear (cone) probe sampling of groundwater was carried out to a depth of 3 m below ground level. Sampling was carried out at 5-m intervals along an 80-m transect of the foreshore (A-B on Fig. 1) and then at 2.5-m intervals near the suspected edges of the plume. Another transect originating from the plume centreline and extending due east 6 m into the river was also surveyed with the spear probe (C-D on Fig. 1). Here samples were

taken at 0.25-m depth intervals. Groundwater samples were recovered from the spear probe using the same technique as for multiports, where the sample is drawn up through nylon access tubing from a small-screened interval at the head of the spear.

Groundwater quality parameters measured at each sample location and depth were the dissolved oxygen concentration (DO), the electrical conductivity (EC), pH and the redox potential (Eh). Groundwater samples taken from the multiport boreholes and spear probe were analysed for benzene, ethylbenzene, toluene, *m*-xylene, *p*-xylene, *o*-xylene, 1,3,5-trimethylbenzene, naphthalene, 1-methylnaphthalene and 2-methylnaphthalene. The organic compounds were concentrated from groundwater samples using solvent extraction techniques, and quantified using gas chromatography-mass spectrometry comparison with an internal standard.

RESULTS

River and Groundwater Hydraulics

River and groundwater levels along the local groundwater flow line have been monitored continuously since July 2000. Changes in the river level indicated tidal ranges of <0.1 m to >0.6 m. Groundwater levels monitored 8 m inland from the river shoreline were very responsive to changes in the river water level (see Fig. 2). Periods of groundwater flow reversal were evident during some high tide events where river water levels exceed those of the near shore groundwater levels (e.g. see 7, 12 and 13 September 2000, Fig. 2). Monitoring probes at 18 m and 50 m inland from the shoreline showed little response (<0.05 m variation) to the changing river conditions.

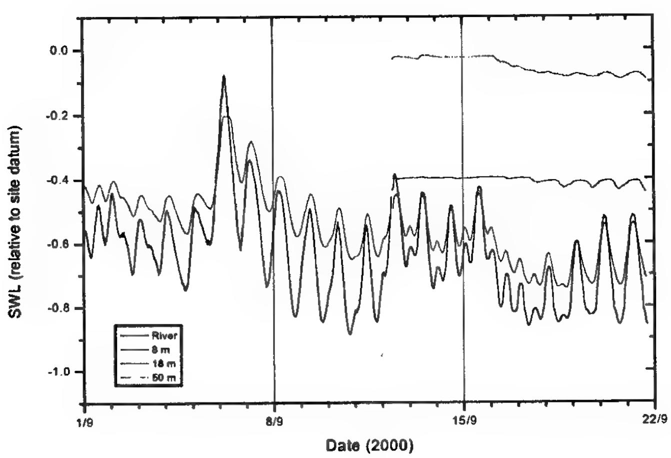

Fig. 2. Standing water levels (SWL – metres relative to datum) from online loggers situated in the river, and 8, 18 and 50 m inland from the river shoreline in September 2000

Depth Profiling

Results from multiport borehole sampling (see Fig. 3) indicated that dissolved hydrocarbon concentrations vary sharply with depth at the site. The top and bottom of the plume and the depths of highest concentration were clearly delineated. At C-MP01, the BTEX compounds occurred between 1.5 and 5.0 m below ground level. In C-MP02, the bulk of the

BTEX compounds and naphthalene occurred between 1.5 and 6 m below ground level. Toluene was below 20 $\mu g\ L^{-1}$ at all depths. Elevated concentrations of xylene (up to 5650 $\mu g\ L^{-1}$) and ethylbenzene (up to 500 $\mu g\ L^{-1}$) were coincident with the high benzene concentration zone. Xylene and ethylbenzene concentrations showed moderate elevation again at 5.5 m, and were also associated with low concentrations of benzene. Figure 3 indicates that the relative concentrations of the benzene, ethylbenzene and the sum of the xylene isomers (BEX) were highly variable down the vertical profile, particularly between 3.5 and 6.0 m. Despite this, over a short tidal period on 17 August 1999, BEX concentration ratios at the 4.5 m depth in C-MP02 were reasonably consistent with time.

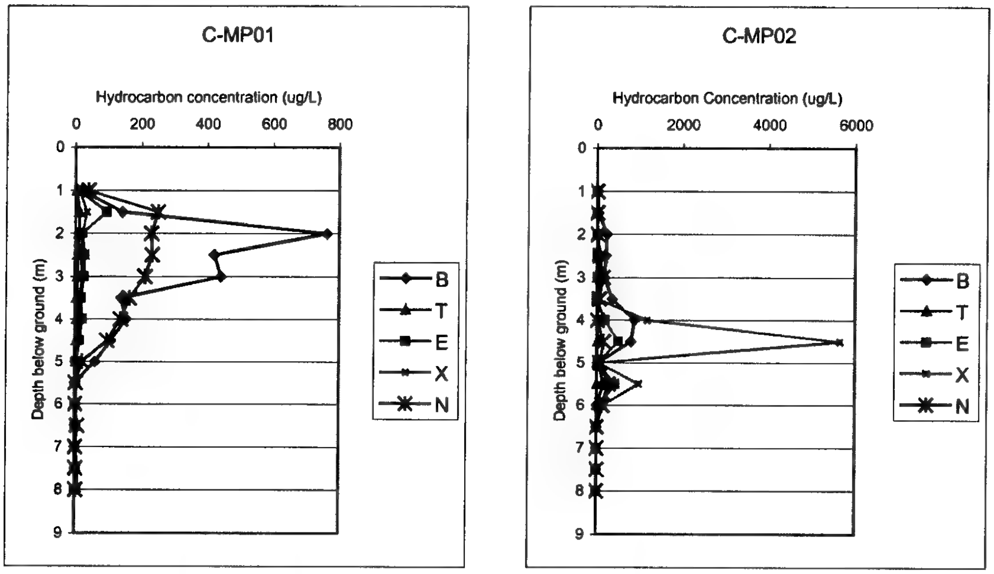

Fig. 3. Depth profile of dissolved BTEX and naphthalene (N) concentrations at C-MP01 and C-MP02 taken 10 August 2000. Note that there is a difference in scales for C-MP01 and C-MP02.

Figure 4 shows depth profiles for the groundwater EC, DO and pH at C-MP02. The EC profile indicates the presence of saline water underlying the fresh groundwater at depths greater than 6.5 m. This trend was also observed in C-MP01. Conductivities of the saline water were up to 50200 $\mu S\ cm^{-1}$ (30120 $mg\ L^{-1}$ TDS), close to that of typical seawater (58000 $\mu S\ cm^{-1}$, 35000 $mg\ L^{-1}$ TDS). Dissolved oxygen concentrations indicate that groundwater was anaerobic (<1 $mg\ L^{-1}$). The pH was between 6.5 and 7.5.

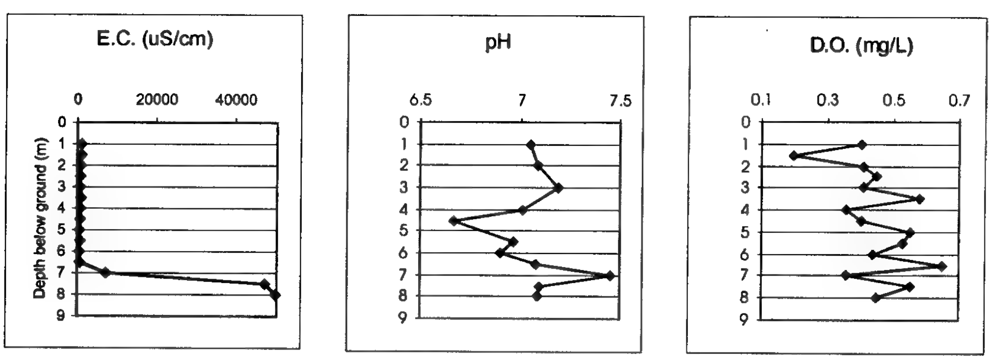

Fig. 4. Depth profiles of selected groundwater quality parameters in C-MP02 measured on 10 August 2000

Plume Width and In-river Extent

Groundwater sampling at 3 m below ground surface along transect line A-B (Fig. 1), perpendicular to the flow axis of the contaminant plume, showed the plume to have a lateral width of 20-25 m (Fig. 5). Both of the multiport boreholes C-MP01 and C-MP02 were 2.5 to 5 m inside the boundaries of the plume. The benzene data in Fig. 5 are consistent with benzene concentrations observed at the multiport boreholes at an approximate depth of 3 m (Figs 2 and 3).

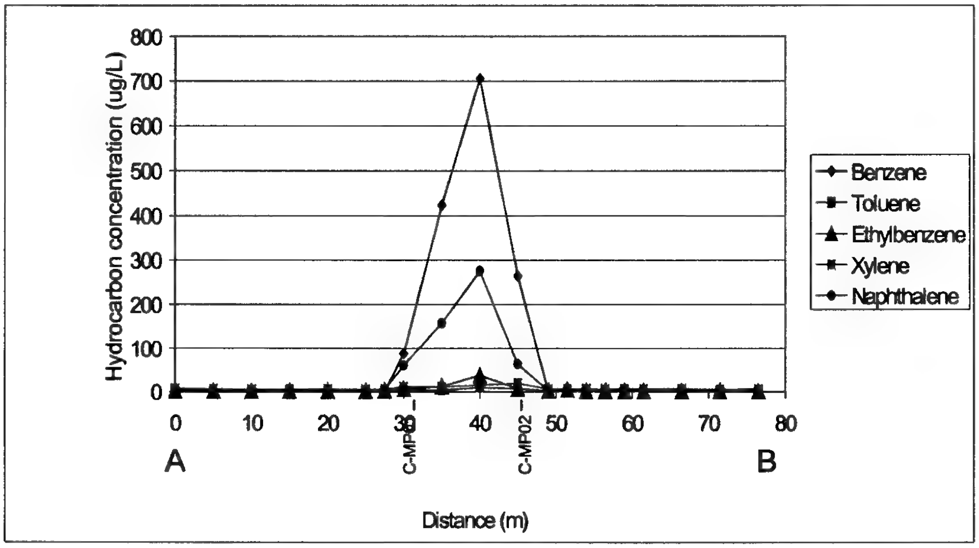

Fig. 5. Profile of selected organics along the river foreshore showing the width of the plume. Samples were taken at depths of 3 m along transect A-B (see Fig. 1) on 14 September 2000.

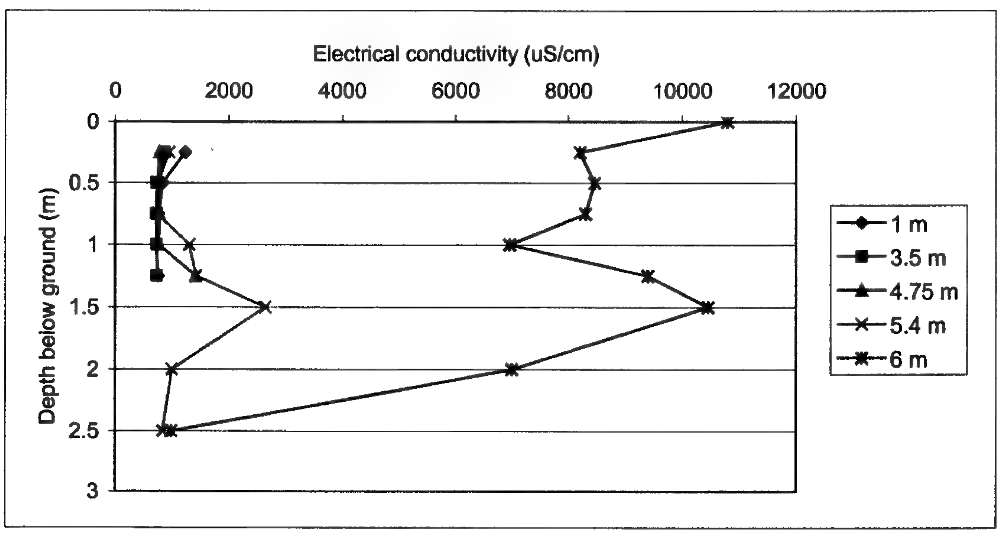

Fig. 6. Electrical conductivity (μS cm^{-1}) depth profiles for sampling locations on transect C-D (see Fig. 1) extending 1 to 6 m from the river shoreline, taken during an ebbing tide.

Groundwater sampling at 0.25- to 0.5-m depth intervals into the river sediments at several locations along transect line C-D, was undertaken during an ebbing tide to give preliminary data on groundwater behaviour as it discharges into the river. The electrical conductivity was used to assess the spatial extent of the groundwater seepage face. Figure 6 shows EC profiles along the C-D transect. A seepage face of fresh groundwater discharge was found to occur as the tide retreated, extending at least 5.4 m into the river from the shoreline. Past the seepage face, it appeared that brackish river water (11000 μS cm^{-1}) had infiltrated the river sediments. General reductions in EC values of the river sediment occurred with depth between 5.4-6 m from the shoreline until fresh groundwater EC values were intersected closer to the shore. At 6 m from the shoreline, brackish water extends to a depth of 2.5 m, indicating increasing depths of river water infiltration and possibly less groundwater input with increasing distances from the shoreline, although at depths below 2.5 m it appears that fresher groundwater was discharging to greater lateral distances than 6 m into the river. This will be investigated during subsequent sampling.

DISCUSSION AND CONCLUSIONS

The use of multiport boreholes for groundwater sampling has enabled clear definition of the vertical distribution of hydrocarbon compounds in a near-shore river environment. Profiles of BTEX concentrations at C-MP01 and C-MP02, both of which are situated proximal to the outer boundaries of the plume, differ both in depth intervals of highest contamination and in relative concentrations of the contaminants with depth. Such lateral and vertical variations across the plume are indicative of complex biogeochemical and/or hydrodynamic processes at work. Transect sampling at a depth of 3 m across the plume showed a plume width of approximately 25 m.

Electrical conductivity recordings taken at the multiports and along transect C-D perpendicular to the shoreline, indicated that two groundwater/river water interfaces or dispersion zones are present: (1) an upper dispersion zone between brackish river water and groundwater, and (2) a lower interface between groundwater and deeper saline water (salt wedge). The upper dispersion zone forms when groundwater percolates upwards through the river sediments and mixes with brackish river water. Based on this initial sampling and assessment, the upper dispersion zone appears to have had a limited lateral extent into the river, at most 6 m from the shoreline above a depth of 2 m. This needs to be further investigated for deeper depths and for other tidal cycles. At low tide, a seepage face is evident where the fresh groundwater discharges to the surface. At high tide, the upper dispersion zone should include the area of seepage.

The lower interface is interpreted to behave as a classical groundwater/saltwater wedge (Reilly and Goodman 1985, Ataie-Ashtiani *et al.* 1999). Density variations between the two water types should result in a zone of diffusion that will drive groundwater and diffused salt water upwards towards the seepage face and upper dispersion zone. The high conductivity of the saltwater wedge relative to the brackish surface river water suggests that this saline water is sourced from ocean water that intrudes the estuary. Turner *et al.* (1996) reported similar findings from investigations of shallow groundwater and brackish river water interaction in the Swan River. EC sampling over the seasonal up-river migration of saline/brackish by Turner *et al.* (1996) showed a large turnover in pore water within the upper 0.6 m of river sediment, while EC values were fairly constant over time below the 0.6 m depth. Recent modelling by Ataie-Ashtiani *et al.* (1999) showed that seawater intrusion into unconfined aquifers dramatically changes the flow pattern and velocity of groundwater near the shoreline, and that tidal activity forces seawater to intrude inland and also causes a thickening of the

interface (compared to non-tidal simulations). Current field investigations show that near shore groundwater levels are tidally influenced. A highly complex and dynamic system is therefore apparent and is likely to vary tidally and seasonally.

The current work-in-progress has involved the preliminary characterisation of a groundwater hydrocarbon plume as it discharges into a river estuary. The long-term objective of the project is to fully quantify and map the short- and long-term behaviour of the groundwater hydrocarbon plume near the river and to identify hydrodynamic controls on plume movement at the groundwater/surface water interface. In particular, the net mass flux of hydrocarbon compounds towards the surface water/groundwater interface will be investigated and quantified, as will the role of redox conditions on the biodegradation of petroleum hydrocarbons in the plume.

ACKNOWLEDGEMENTS

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Influence of a Drainage Network on the Dissolved Substances Transport in an Environment

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ABSTRACT: A basic function of agricultural drainage is to create an optimum water-air-soil regime for soil tillage and plant growth. At the same time the role of drainage is important in circulation of various elements and compounds which are transported by water in the dissolved form. In this paper we consider the negative and positive aspects of chemical substances leaching by drainage discharge. We report the results of modelling the transport dissolved substances in drained soils of northwest Russia. The model takes into account a filtration of solutions through soil flow in a drainage system and river. Recommendations for natural or artificial remediation of polluted soil with the help of drainage are presented.

KEYWORDS: closed drainage, groundwater, soil, fertilizers, remediation

INTRODUCTION

The large share of agricultural fields of northwest Russia needs a closed drainage network because precipitation exceeds evapotranspiration. For the last 30-40 years the construction of closed drainage systems was actively conducted. Also nutrients (organic and inorganic fertilizers) and pesticides have increased substantially during the past 3-4 decades. However, the use of chemicals poses a potential threat to the environment and human health. Therefore environmental scientists are concerned with the fate of chemicals in agro-ecosystems. In the same time have begun the research of closed drainage influence on soil, groundwater and surface water quality (Duffy *et al.* 1975, Lake and Morrison 1977, Jury 1978, Tanji *et al.*1979). Large volume of the information describing this influence today is saved. Such data are essential to the development of appropriate management technologies for minimising nonpoint and/or point source loading of chemical compounds from croplands.

A basic function of agricultural drainage is the creation of an optimum water air soil regime for soil tillage and plant growth. At the same time the role of drainage is important in the circulation of various elements and compounds which are transported by water in the dissolved form. Closed drainage usually is considered to be a production practice rather than management practice for environmental protection. However, artificial subsurface drainage has the potential to change the state of agricultural fields (Baker and Johnson 1976, Baker and Johnson 1983). This change consists in the following: (a) the redistribution of water balance, (b) changes of physical and chemical soil properties, (c) subsidence of groundwater table. The redistribution of water balance consists of decrease of surface runoff and increase of subsurface runoff, that transforms to drainage discharges. As a result the maximum peak of river discharge decreases and high water is stretched. The artificial drainage increases percolation, infiltration volume and changes the regime of soil water content. These factors have an effect on physical properties of soil. These properties are bulk density, differential porosity etc. Listed changes have an effect on circulation of various elements and compounds in an environment. Flow rate of dissolved substances, volume of these substances stored in soil and transported from agricultural lands by erosion, runoff and leaching are changed.

Closed drainage has both positively and negatively influenced the environment (Zwerman *et al.* 1972, Bolton *et al.* 1970, Gast *et al.* 1978, Baker and Johnson 1981). It is necessary to note that closed drainage systems, under condition of decrease of negative influence, can serve the management practice of environmental protection.

The objective of this paper is to summarise from an environmental perspective, the closed drainage problems attributed to contaminated sites, the approaches to the solution that have evolved over the past 3-4 decades, and some of the issues that have emerged and still must be addressed in solving the problems.

The following tasks were put: (a) to generalize available research data, (b) to develop the model of transport and transformation of elements and compounds in soil, groundwater, drainage and surface waters, (c) to develop principles and methods of closed drainage use for environmental protection and contaminated site remediation.

OBJECTIVES OF RESEARCH AND METHODS

Field and laboratory research were conducted from 1970 till 1990 on drained agricultural fields in basins of the Ochta, Mga, Strelka, Izhora, Slavyanka, Kikenka in Leningrad region. Hydrological, hydrochemical and hydrophysical regime of soil, groundwater, drainage and surface water ware observed. Physico-mechanical and physico-chemical properties of soil were defined. These properties are bulk density, porosity, grain size, cation exchange capacity and other. Pore solution was extracted with centrifuge. Water samples from drainage wells, drainage collector outlets, channels and rivers ware taken. Soil tillage, method of chemical application, timing of application and chemical formulations were checked.

Process modelling of transport, transformation and accumulation of chemical substances consider convective-diffusive flow in porous medium, sorption on soils, decay and disintegration, plant uptake, cation exchange, biological transformations and chemical reactions. The rate of water flow in soils is a result of: (a) the driving force, which is the change in water potential per unit of distance, and (b) the hydraulic conductivity (K), which is the ability of the soil to transmit water (unit of distance/time). These factors are related by a form of Darcy's law and convective- diffusive equation:

$$\begin{cases} \dfrac{\partial W}{\partial t} = \operatorname{div} K(\operatorname{grad} P + \rho g) & W = f(P) \qquad K = f(P) \\ \dfrac{\partial WC}{\partial t} = \operatorname{div}[D \operatorname{grad} C - VC] & D = (D_m + \lambda|V|) \end{cases} \tag{1}$$

W – soil water content, K – hydraulic conductivity, P – pressure of soil water, ρ – water density, C – chemical concentration, D – coefficient of hydrodynamical diffusion

At every time interval take into account cycles of transformations of considered dissolved substances. For example Fig. 1. outlines the diagram nitrogen transformations in soils.

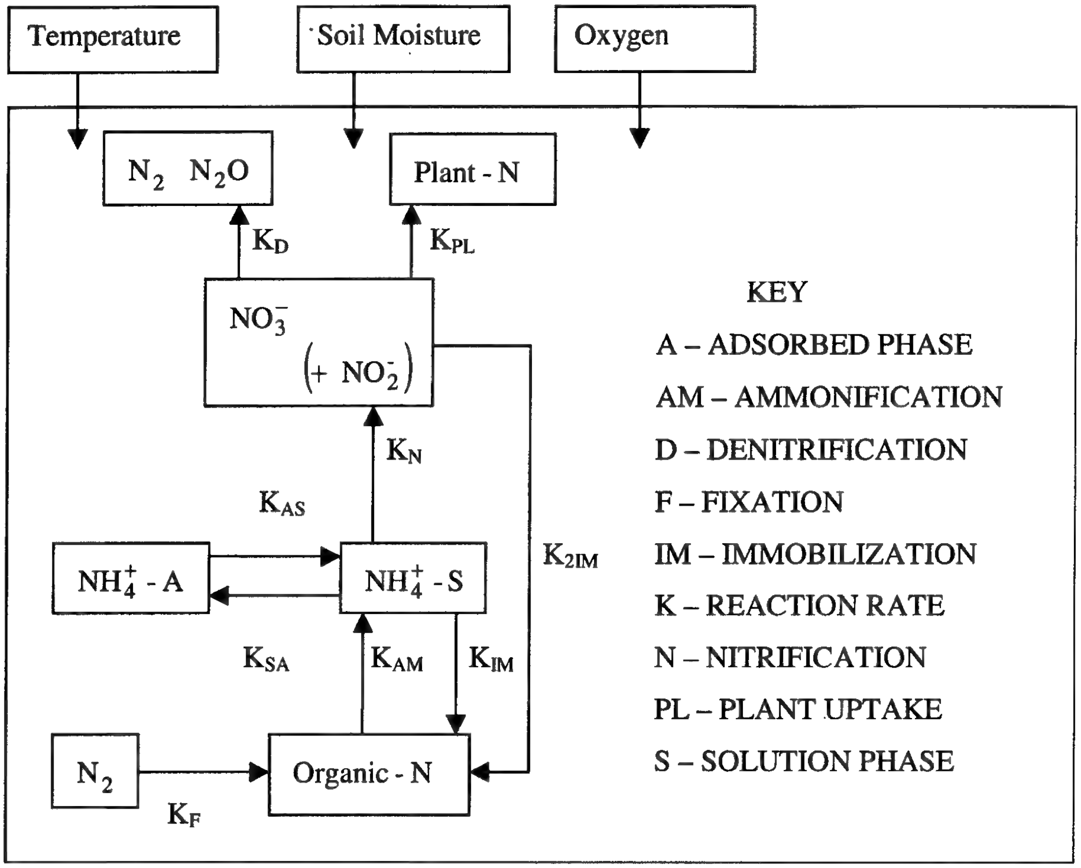

Fig. 1. Nitrogen transformations in soils. (Reproduced from Schaller and Bailey 1983)

RESULTS AND DISCUSSION

When there is not closed drainage a large share of dissolved nutrients and pesticides leave agricultural fields by surface runoff. This event as a rule is short. Also soluble pollutant are leached into the soil. They can move on through the soil and reappear in surface flow downslope, or be leached to the groundwater table. Owing to low rate of flow leached compounds participate in a transformation cycles and accumulate in soils.

Let's consider nitrogen cycle in system: solid phase of soil – pore solution – pore air – biological phase of soil in soil layer from closed drainage level up to surface. It is known, that the nitrogen cycle is defined by many factors: temperature, soil water content, oxygen, physico- chemical properties of soil, soil tillage, method of chemical application, rate of application, timing of application, chemical formulation and other. It is very difficult to predict NO_3^- NO_2^- and NH_4^+ concentrations in the soil profile and drainage effluents in soil.

Research demonstrates when precipitation exceeds evapotranspiration the convective-diffusive flow of water and dissolved nitrogen compounds down is observed. Rate of ion transport through vadose zone depends on difference of precipitation and evapotranspiration. Change of percolating water volume, physico-chemical soil layer properties distinction and time intervals between chemical applications cause essential distinction of ion concentration in soil layers with depth. The maximums and minimums of concentration move down translational through the unsaturated zone to groundwater table. About 90% of the dissolved substances reaching groundwater get in drainage pipes. Time of ion transport through unsaturated soil is 1-3 years and more. Thus influence of fertilizers and pesticides application

on drained soils can have long-term consequences. Closed drainage reduces the length of subsurface water flow paths to an open channel and reduces the time of travel. The duration and degree of anaerobic conditions related to water saturation would also be decreased with closed drainage. Both of these effects would decrease the chance for denitrification to occur and further increase NO_3^- losses by leaching. The reaching time of an open network by polluting substances on 3-4 orders exceeds migration time of these substances without closed drainage. Closed drainage systems conduce to more NO_3^- losses by leaching.

CONCLUSIONS

In small watersheds agricultural fields are considered as the nonpoint sources of environment pollution. The drainage intercepts a large part of infiltration water and dissolved substances, in a soil layer from a level of drainage up to a ground surface. Thus, the drainage protects underlying groundwater from penetration of polluting substances, and also provides soil remediation, reducing accumulation of these substances in soil. It is necessary to note that in watersheds scale, outlets of drainage collectors represent point sources of pollution. The substitution of the nonpoint sources of pollution (agricultural fields) by point sources (outlets of drainage collectors) can conditionally be considered as substitution in a model of filtration through isotropic dispersive medium by a filtration through fractured rock. The transformation of a pollution source from nonpoint to point allows you to locate drainage water for water clearing if that is necessary.

Closed drainage can be used for contaminated agricultural, industrial and urban sites remediation. It is possible to combine closed drainage and irrigation for faster remediation of soil.

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Application of Screening Level Models to Ecosystem Monitoring

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ABSTRACT: Ecosystem monitoring has a variety of objectives dependent on the purpose of the study. The ecosystem risk is dependent on the combined exposures to the community and the community's response to the stressors. The objective of this paper is to illustrate the use of screening level models for the purpose of estimating both the individual chemical constituent concentration and estimated chemical mass flux. This information can then be used in designing monitoring systems and suggesting the required sensitivity of the monitoring equipment.

KEYWORDS: analytical element, analytical, stochastic convective, flux, concentration

INTRODUCTION

Optimal design of an ecosystem monitoring system requires an estimation of the chemical fluxes and contaminant concentrations that will stress the ecosystem. As a general rule the question the monitoring system is attempting to answer is the impact of chemicals on a variety of organisms. At sub-lethal doses, immediate ecological responses frequently cannot be detected. The ecological response is observed after long-term sub-lethal exposure. This suggests a need for chemical monitoring as well as ecological monitoring. Techniques have been developed to estimate risk based on organism exposure to contaminants. The objective of this paper is to demonstrate the application screening level models to estimate the flux and concentration of chemicals that might be expected to expose organisms of concern (i.e. surface water organisms). With finite budgets, not all environmental insults can be addressed. Screening level forecasts followed by risk analysis can set priorities to address the most critical exposure first.

Two examples are presented. First, the anticipated aquatic exposure to methyl tertiary butyl ether (MTBE) resulting from a fuel spill at a service station in Port Hueneme, California USA. The second example looks at the effect of installing a soil cap on contaminated stream sediments and how the cap modifies the contaminant flux into the stream requiring significant changes in the monitoring strategy. No verification data are currently available to evaluate performance of the modeling approaches. At Port Hueneme, a decision was made to cut off the MTBE plume before it reaches surface water. A field site for the sediment cap scenario has not yet been selected. The results presented are for a hypothetical example.

METHODS

Aquatic Exposure to MTBE

For the Port Hueneme example, a stochastic approach following the theory of Jury and Heuvelman (Heuvelman and McInnes 1999, Jury and Scotter 1994, Jury *et al.* 1982) was developed. Numerous studies have looked at distributions of hydraulic properties of soils as a function of space. A classical example is given in Nielson *et al.* (1973). They suggest that the

distributions of hydraulic properties in the field follow log normal distributions, which was the transfer function selected to describe water movement at Port Hueneme. In recent years, several studies have been conducted to study the degradation of MTBE under natural conditions (Borden *et al.* 1997, Bradley *et al.* 1999, Butler *et al.* 2000, Church *et al.* 1999a, Church *et al.* 1999b, Happel *et al.* 2000, Javanmardian and Glasser 1997, Landmeyer *et al.* 1998, Mackay *et al.* 1999; Mackay *et al.* 2000, Salanitro 2000, Salanitro *et al.* 1999, Schirmer and Barker 1998, Schirmer *et al.* 1999, Wilson *et al.* 1999). The general consensus is that MTBE will degrade biologically under aerobic conditions but be relatively stable under reducing conditions. At Port Hueneme, the aquifer conditions are reducing and it was assumed for the modelling activities that the MTBE would not degrade. The monitoring activities, however, would likely want to evaluate potential transformations at groundwater surface water interfaces following the work of Bradley *et al.* (1999) and determine if extraction or *in situ* remediation were essential or if there is a significant potential for natural attenuation at this interface.

With no chemical degradation in the aquifer, the stochastic problem is reduced to a convective-transport problem. The reactions at the groundwater surface water interface were not modelled. The stochastic-convective hypothesis physically states that solute travels purely by convective flow in isolated stream tubes without mixing. Each of the stream tubes has uniform properties within it, but the properties vary from one tube to the next. A transfer function is then used to describe the properties of the stream tubes. The foundational basis of transfer function modelling is the principal of superposition. With this assumption, a solution to a nonuniform initial or boundary value problem can be built up from the impulse response function describing the distribution of solute following the addition of a narrow-pulse input of chemical to the system. The solution to the field scale problem is equal to the ensemble average of the solutions to the tube-scale transport problem.

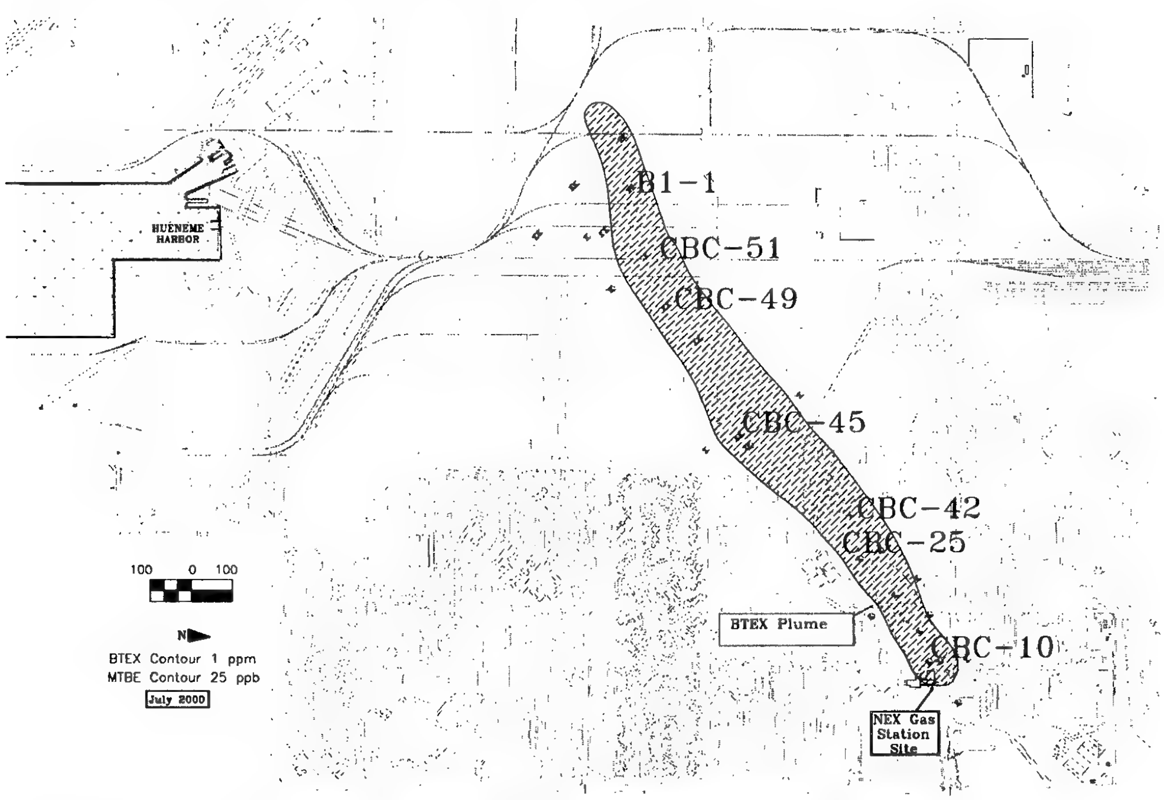

Fig. 1. Plan view of Port Hueneme showing MTBE plume and selected monitoring wells

Figure 1 shows the MTBE plume at Port Hueneme as of June 2000. This plume was generated from the accidental release of approximately 42000 L of fuel lost some time in 1985. The volume of the release was estimated based on station records. The in-ground fuel tanks, distribution system and contaminated soil were removed from the site shortly after the release was detected. For this reason, it was assumed that all of the remaining NAPL is at the water table and the NAPL formerly in the vadose zone was removed and not considered in the evaluation. The unconfined surficial aquifer is a relatively permeable aquifer underlain by a low permeability clay unit. The water table is approximately 3 m above the top of the clay unit. It is believed that the contamination is confined to the surficial unit since the downward gradient through the clay at the bottom of the contaminated material is small. However, routine sampling below the clay unit has not been performed. The climate is arid with little recharge and much of the surface is relatively impermeable with parking lots and buildings where the surface events are not allowed to infiltrate significantly nor is there a significant amount of evapotranspiration. The hydraulic gradient at the site, 0.001 to 0.003 m m^{-1}, is reasonably stable. No pumping wells are currently active in the area. The water in the aquifer is brackish and not suitable as a water supply. The environmental concern, therefore, is the potential contamination of surface waters and organisms that reside in the surface waters. The objective of the study is to forecast the chemograph that potentially may be released to the drainage ditch shown at the top of Fig. 1 and to estimate the temporal mass flux that might enter the surface water. This would permit developing a monitoring strategy for the drainage ditch. Researchers have hypothesized that as the water passes through the sediments a significant amount of the MTBE may degrade in the high organic material at the groundwater surface water interface (Bradley *et al.* 1999). The ideal approach would be to allow this process to naturally attenuate the contaminant rather than perform some aggressive remediation due to the type of water that exists. The natural attenuation taking place in the formation is primarily mass transport with little if any transformation. There is no assurance that these sediments will be effective in achieving the desired objectives. It is, therefore necessary to design a monitoring system that is capable of detecting the performance of this sediment layer for MTBE removal. As well, a plan is required to intercept the plume if the surface sediments are unable to adequately transform the MTBE.

At the time of the release, MTBE was not being added to fuels to meet air quality objectives but probably included in some of the fuel as an octane booster. A typical amount of MTBE used as an octane booster in premium fuel is 3%. When the release occurred, MTBE was not considered an environmental issue and measurements were not made to determine the MTBE concentration in the released NAPL. Without knowledge of the volume fraction of MTBE, forecasting of the plume duration can be bracketed assuming the volume fraction is between 0 and 3%. Monitoring wells have been installed that permit delineating the location of the plume. Wells labeled on Fig. 1 have been monitored several times and permit watching the recent temporal history of the plume. Figure 2 displays a snapshot in time (October 1999) the concentration along the plume. The concentration in one well, CBC10, was adjusted up to the concentration that had been observed prior to recent samplings that are beginning to show a decline in the MTBE concentrations. The reduction in concentration is believed due to the natural flushing of the sediment by MTBE-free water entering the area discussed later. By plotting the concentration at a value previously observed, the resulting plot looks as if there was a continuous source of MTBE. This data can be used to estimate the mean interstitial velocity and standard deviation of the interstitial velocity assuming a lognormal distribution for the travel time.

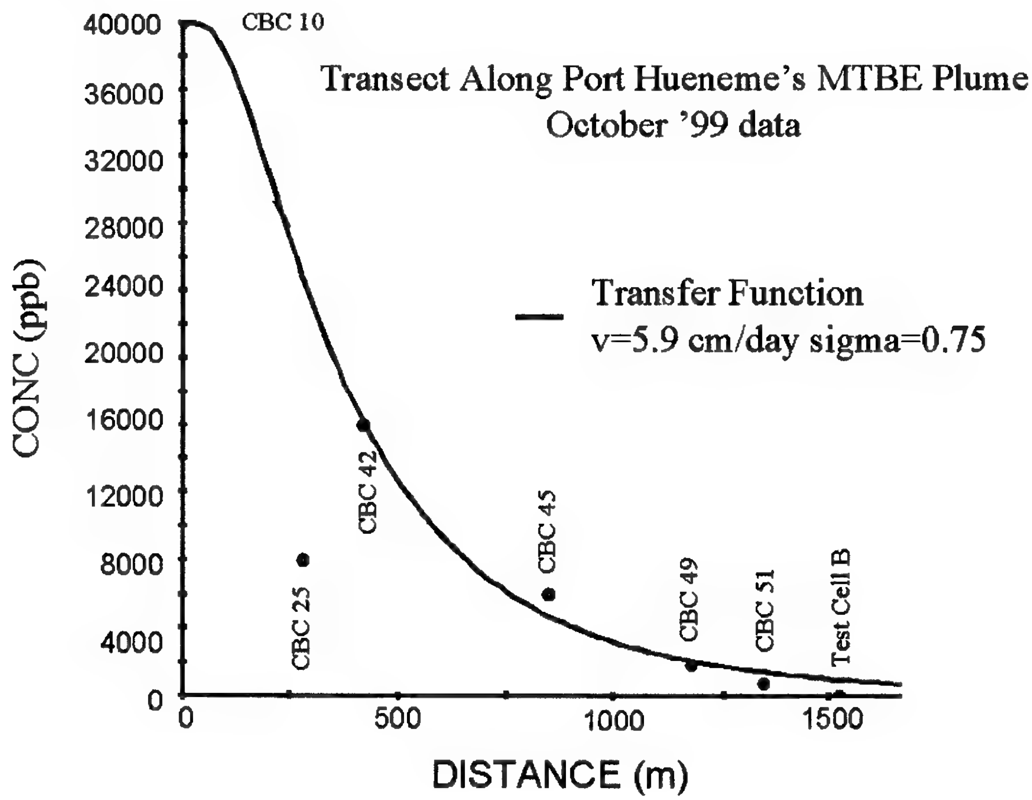

Fig. 2. MTBE transect along the flow path collected 15 years after release of the fuel

In Fig. 1 there is a contour for the 1-ppm level of BTEX. The area enclosed by this contour is significantly larger than the NAPL source zone. If one defines the source zone as the area where the NAPL concentration is 5 kg m^{-2} (J.T. Wilson pers. commun. 1999) and assumes the density of the fuel is 0.9 g cm^{-3} and the volume of the release is 42000 L then the area occupied by the spill is 7500 m^2. If the aspect ratio were 2:1, then the dimensions of the spill would be approximately 60 m x 120 m. The effective porosity for the formation is expected to be 0.2. Typical residual NAPL saturation for an LNAPL in this kind of formation material is approximately 5% of the porosity. With the assumed release volume and aquifer properties, this would suggest a smear zone thickness of about 0.6 m. The aquifer at the source zone is approximately 3 m thick. Assuming the formation is homogeneous we can calculate the apparent average mass fraction of MTBE in the fuel to generate 40 mg L^{-1} observed in the monitoring wells within the source zone. The calculated mass fraction of MTBE is 0.4%. This is in the range of the 0 to 3% anticipated. It is known that the bottom of the aquifer is more permeable than the top of the aquifer (E. Lory pers. commun. 2000). This would suggest that the actual average mass fraction of MTBE is actually greater than the value calculated.

Since each of the flow tubes is assumed to have the same NAPL saturation, it is easy to quantify the number of solution volumes that are required to dissolve the MTBE. Approximately one solution volume of water would be required to pass through the NAPL zone to dissolve the MTBE. Using this information a forecast can be made that permits designing the monitoring system.

Monitoring of a Contaminated Sediment Cap

Groundwater and surface water are interconnected. As rain or snow falls to the earth's surface, some water infiltrates through soil into aquifer and some runs off the land to rivers, lakes, streams and oceans. Some water can intrude from those surface water bodies into the subsurface and reach groundwater. Over time groundwater travels down gradient and discharges into surface water at locations where the water table intersects the surface topography. Because groundwater and surface water are intimately linked through the hydrologic cycle (Domenico and Schwartz 1990), knowledge about hydrologic interactions between them is critical to understanding the movement of water and pollutants in the environment.

Contaminants are transported because of groundwater flow and concentration gradients. In sediment capping sites, theoretical calculations based on molecular diffusion only, often suggest it would take more than hundreds of years for pollutants to break through a sediment cap. Although advective flux may significantly affect capping effectiveness, groundwater discharges at sediment capping sites are seldom evaluated. The second example hereafter illustrates a screening level process that couples a regional groundwater flow model, GFLOW, and a sediment cap evaluation model, SCAPE, to investigate capping effectiveness in a river under conditions of groundwater discharge. It also shows how this information can be used in designing ecosystem monitoring. Since this example intends to demonstrate the process rather than the true results of a field study, a hypothetical site near Vincennes, Indiana is chosen for this exercise. The pollutant present is assumed uniformly distributed in a section of the Wabash River sediment and is persistent in the environment.

GFLOW, developed by the Haitjema Software, is an analytic element model (Haitjema 1995, Mitchell-Bruker and Haitjema 1996) solves conjunctive steady state groundwater and surface water flow. GFLOW allows display of binary base maps for streams, lakes, roads, legal boundaries, etc. A map of all surface water features is called a hydrography map. In order to translate a hydrography map into boundary conditions for the groundwater flow model, water levels along streams, creeks, and in lakes must be known. Streams and lakes are represented by strings of straight linesinks with each assigned a head that is set equal to the water level in the stream or lake. Linesinks are sink distributions along straight line elements used to model stream and lake boundaries. In this example, head-specific linesinks from the up gradient end of the streams to the down gradient end are created and interconnected as a streamflow network (Fig. 3). The aquifer properties and recharge rate are assumed homogeneous in the model area. The inhomogeneity, horizontal barrier and pumping well features were not used in this example for simplicity. The unconfined aquifer base is set at 100 m above sea level, the hydraulic conductivity is 15 m day^{-1}, the effective porosity is 0.2, and the recharge rate is 0.15 mm day^{-1}. Resistance was added to the Wabash River to represent the existence of a less permeable sediment layer between the surface water and the aquifer. Resistance is the thickness of the low permeable layer underneath the river divided by the vertical hydraulic conductivity, and is set equal to 5 days. The width of the river is 177 m and the distance between the surface water elevation and the bottom of the resistance layer is 4.6 m. The contaminated sediment and cap is within the rectangular area ABCD as shown in Fig. 4. The model generates contour plots of equipotentials and computes the piezometric head and groundwater discharge strength of each assigned linesinks. Solution accuracy is verified by comparing computed heads to locations at which the groundwater elevation or piezometric head is known.

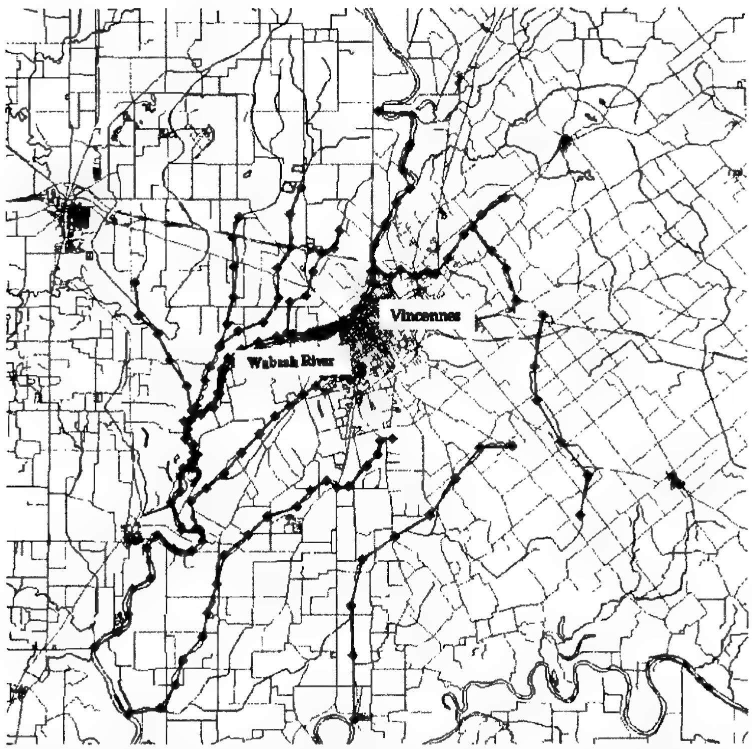

Fig. 3. Head-specific linesink network in the area of Vincennes, Indiana. Wabash River is 177 m wide, therefore linesinks were positioned along both sides of the river to improve the realism of the model.

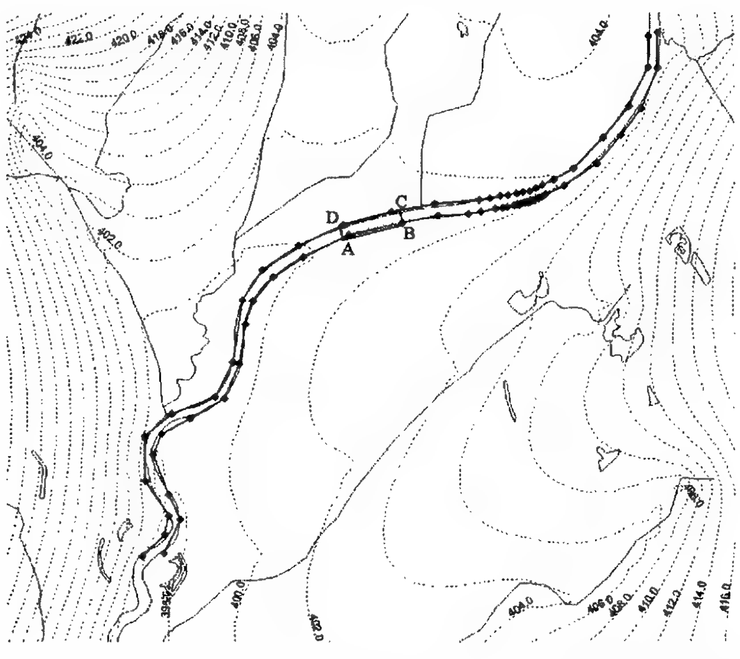

Fig. 4. Contours of equal piezometric head in the area of Vincennes, Indiana. The contaminated sediment and cap is within the rectangular area ABCD in the Wabash River.

SCAPE is a beta version of sediment cap evaluation model developed by U.S. EPA's National Risk Management Research Lab. It is based on the analytical solutions (Freijer *et al.* 1998) of the convection-dispersion transport equation (Enfield 1985) under certain assumptions and boundary conditions. The model describes fate and transport of pollutant in

contaminated sediment overlaid by a clean cap with same physical and chemical properties. It is assumed that the fluxes move one-dimensionally upward and the groundwater discharge is free of contaminants. It is also assumed that there is no concentration gradient at infinite distance. The model projects and displays the relative concentration distribution in the sediment profile at any specified time from time zero. It also calculates the contaminant fraction remaining in the sediment at the given time. The input parameters include pore water velocity, dispersion coefficient, degradation rate constant, porosity, bulk density, organic carbon content in sediment, organic carbon/water partition coefficient, thickness of contaminated sediment and thickness of overlaid clean sediment. In this example, all input values used to run the model were hypothetical and were displayed along the plot of concentration profile as shown in Figs 8 and 9. Two sets of condition were simulated to evaluate the effect of advective flux on 2 m of contaminated sediment overlaid by 1 m of clean cap. One scenario included both advective and diffusive fluxes and the other considered diffusive flux only. The advective flux value was obtained from the GFLOW simulation. Note that the degradation rate constant is set to a very small number since the pollutant is assumed persistent in the environment and the main focus of the evaluation is on the effect of advective flux.

RESULTS

Aquatic Exposure to MTBE

The estimated interstitial velocity at Port Huemene's MTBE plume is 6 cm day^{-1}. This was obtained by fitting, using the method of least squares, the response of a step function to a lagrangian solution of the stochastic convective model as shown in Fig. 2. The standard deviation of the travel times was also determined to be 0.75.

Illustrated in Fig. 5 is the anticipated breakthrough curve 1800 m down gradient from the spill. To calculate this curve, we assumed that: the NAPL source area was 120 m in length; the mean interstitial velocity is 6 cm day^{-1}; the standard deviation in interstitial velocity is 0.75; the NAPL is uniformly distributed in each of the flow tubes at the source area; the solubility of the MTBE is 51 g L^{-1}. The solubility impacts the number of pore volumes required to dissolve the MTBE from the NAPL. The calculation was made based on an assumed source area length of 120 m and a requirement of one solution volume to dissolve the MTBE. For Fig. 5, this is the same as applying a pulse of chemical for 0.07 pore volumes. The figure displays the results based on pore volumes as well as elapsed time from the chemical release. One observes some oscillation in the projected curve. The oscillation is a result of the number of flow tubes. One thousand flow tubes were used in the calculation that results in a numerical precision of 0.1% of full scale. The projection suggests that the maximum concentration should occur approximately 80 years after the release and low concentrations should be currently detectable at this location.

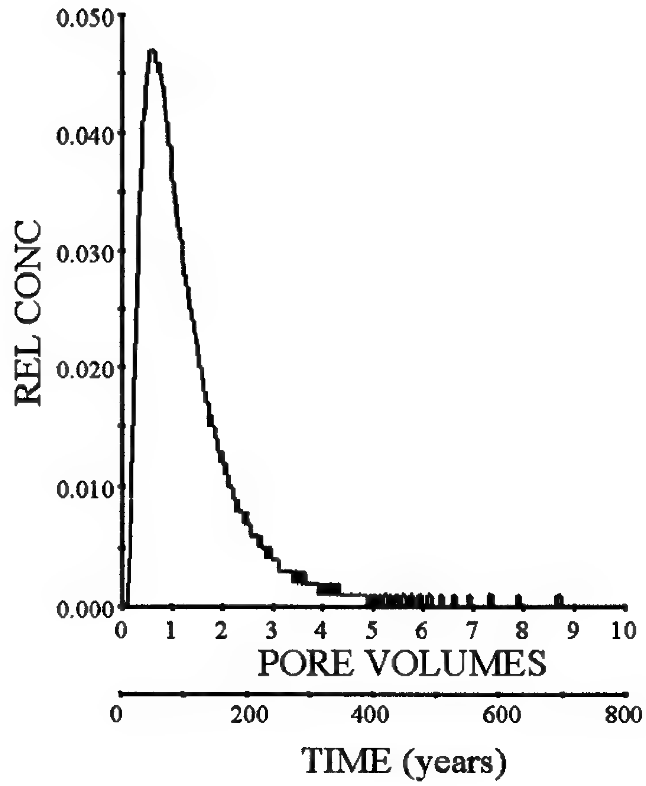

Fig. 5. Projected elution curve 1800 m down gradient from the source

At the source area it is also possible to estimate when the concentration should begin to decline just due to dissolution. This information is valuable as part of the monitoring strategy since it will give information on possible adjustments that might need to be made. Figure 6 illustrates the anticipated decline in concentration at the down gradient end of the source zone.

Similar to Fig. 5, Fig. 6 displays both pore volumes and years after fuel release. The calculations are based on the results shown in Fig. 2 and assumed the source area is 120 m along the flow path. The figure suggests that there should be significant reductions observed in the MTBE concentration at the present time. Observations as mentioned earlier are consistent with the projections.

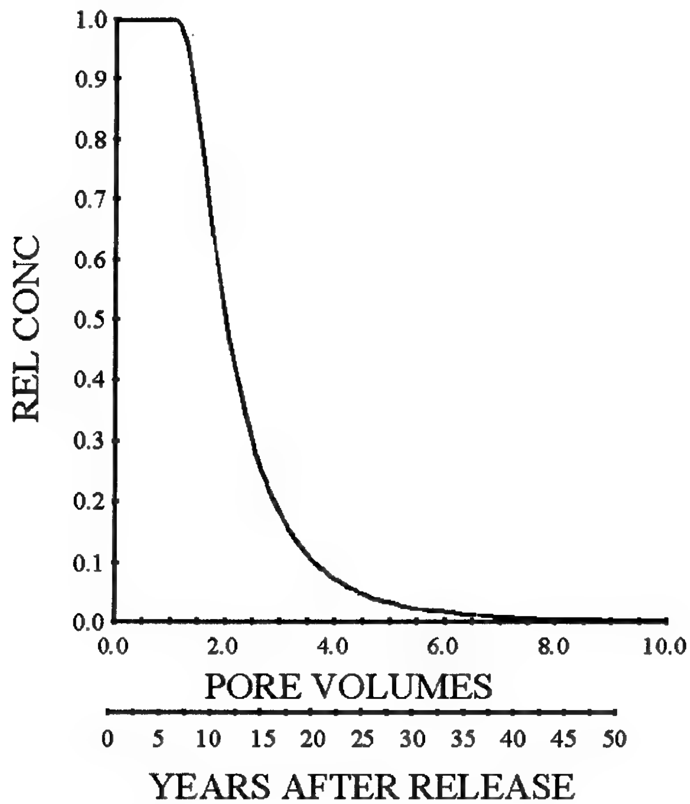

Fig. 6. Projected source zone concentrations

Monitoring of a contaminated sediment cap

Contours of equipotentials are plotted on top of the hydrography map after the groundwater solution is created (Fig. 4). Overall error in head is 0.002% after five interations. It is evident that Wabash River is a gaining stream (Fig. 7) because the equipotentials' 'V's point upstream and groundwater flows down gradient toward both sides of the river. Since the area of interest is focused on the contaminated zone ABCD, the groundwater flux into the area must be determined. GFLOW-estimated discharge strength into linesink AB and CD is 3656 and 1293 cm^2 day^{-1}, respectively (discharge strength is defined as the discharge rate into the linesink in volume per day per length of linesink). Hence, the combined discharge strength into ABCD is 4949 cm^2 day^{-1}. Dividing this number by the width of the river, the groundwater flux into the contaminated area was determined as 0.28 cm day^{-1}. This specific information, besides being subsequently useful in the SCAPE model, suggests the required sensitivity for the benthic flux measuring device if such measurement is to be made in the field.

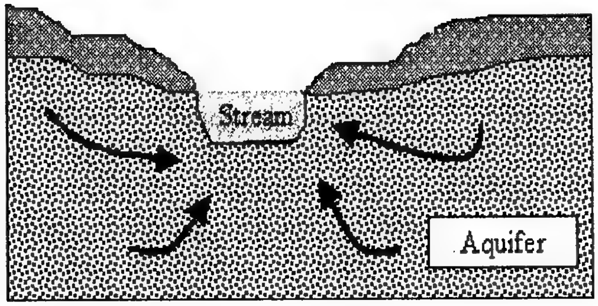

Fig. 7. Streams gain water when the stream surface elevation is below the surrounding water table

Groundwater flux of 0.28 cm day^{-1} was converted to pore water velocity of 0.008 m day^{-1} for SCAPE input. The assumption was made that groundwater mainly discharges vertically upward through the sediment into the surface water. Discharge through the riverbank into the water column is negligible. Figure 8 shows the vertical concentration profile when both groundwater discharge and molecular diffusion were included in the simulation. The dotted line represents the contaminated/clean sediment interface. After 1000 days, 17.7% of the contaminant was released into the water column. The relative concentration at the cap/water interface is high at 0.95. The overlaid clean cap is almost fully contaminated with maximum concentration. Not only surface water organisms are exposed, the bottom filter feeding species are also at risk. However, it does not necessarily imply the ecological community is stressed. It all depends on how the community responds to the stressor. Still, the modelling results address potential ecological risk and provide valuable information for designing optimal monitoring systems based on the flux and concentration of contaminant. Figure 9 presents the vertical concentration profile when groundwater discharge was excluded in the simulation. The results are noticeably different from the previous one. After 1000 days, the pollutant is still fully contained. The surface water organisms are not exposed and the bottom filter feeding organisms are not at risk either. The distinctly different results indicate the importance of groundwater discharge in affecting the sediment capping efficiency. A groundwater flux of only 2.8 mm day^{-1} significantly magnified risk exposures to the ecological environment.

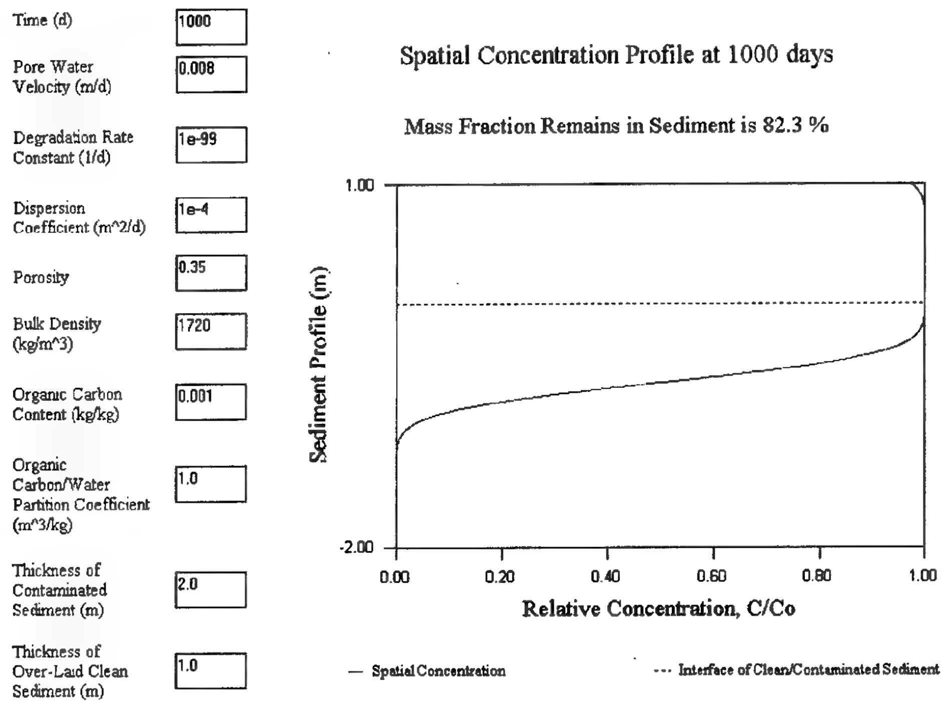

Fig. 8. When included both advective and diffusive fluxes, SCAPE projects the pollutant breaks through the cap and the contaminant fraction remains in the sediment is 82.3% after 1000 days. The dotted line is the clean and contaminated sediments interface.

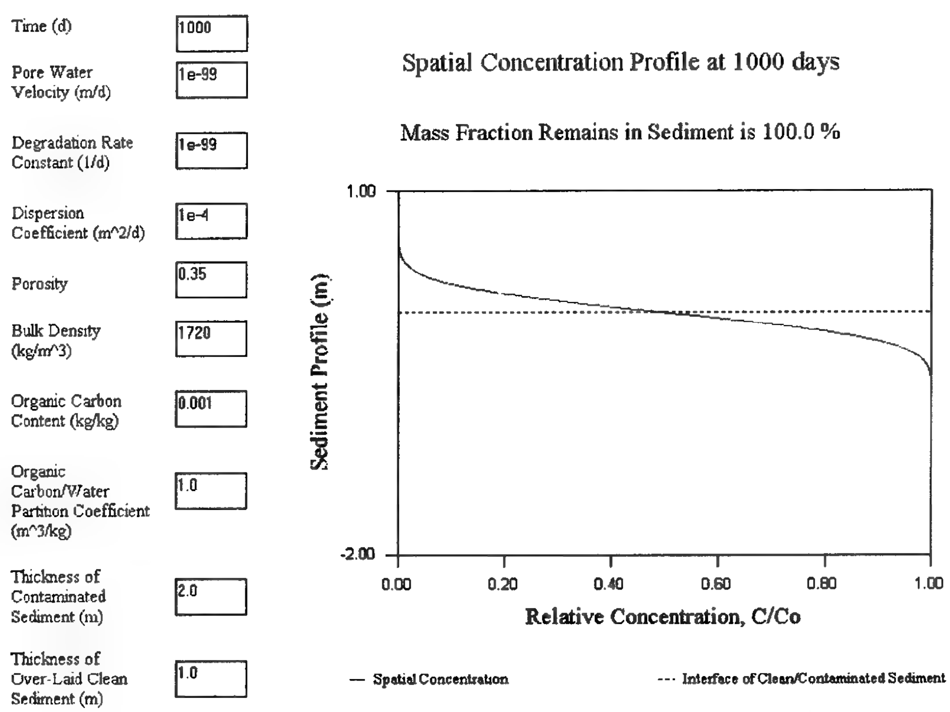

Fig. 9. When excluded advective flux, SCAPE projects the contaminant is fully contained after 1000 days. The pollutant is far from breaking through the cap. The dotted line is the clean and contaminated sediments interface.

DISCUSSION

Aquatic Exposure to MTBE

Many assumptions were made during the modelling projections. The purpose for the modelling was to determine the level of sensitivity that would be required if an environmental monitoring system were to be installed. From Fig. 5 we can see that the maximum expected relative concentration for MTBE is approximately 0.045 or almost 2 mg L^{-1}. If degradation takes place at the groundwater surface water interface as is anticipated, the concentration entering surface water should be less than 2 mg L^{-1}. It is likely that if degradation takes place the daughter product tert-butyl-alcohol (TBA) will be observed. This parameter should be included as part of the monitoring plan. California has proposed a drinking water standard of 5 $\mu g\,L^{-1}$ and individuals can taste MTBE at approximately 15 $\mu g\,L^{-1}$. These levels are significantly below the anticipated maximum concentration potentially entering the surface waters. With a 3 m thick aquifer and effective porosity of 0.2 and an interstitial velocity of 6 cm day^{-1}, the expected mass flow is 0.036 $m^3\,day^{-1}$ per metre width of plume. The peak contaminant mass flux is then expected to be 0.072 g $day^{-1}\,m^{-1}$ plume width.

Monitoring of a Contaminated Sediment Cap

Field data such as hydraulic conductivity, groundwater discharge/recharge, contaminant distribution, etc. are not generally known with a high degree of accuracy. At best, modelling can only lead to some possibilities within which we expect the actual values to occur. Sensitivities to selected parameters can be evaluated to suggest critical monitoring parameters. If some of the most sensitive parameters are overlooked, the potential ecosystem at risk may not receive proper monitoring. When projecting capping effectiveness, groundwater discharge is seldom evaluated. In this paper, a screening level process model coupled with a groundwater flow model was used to evaluate a sediment cap. The model demonstrated the sensitivity of groundwater discharge in cap performance. The modelling exercise illustrated the need to carefully monitor the ground water surface water flux at cap sites. In summary, it is obvious that knowledge of the regional hydrologic interactions is essential for local sediment cap effectiveness to be evaluated correctly and the ecosystem monitoring be designed optimally.

CONCLUSIONS

Two different approaches using screening level models were used to provide insight into the anticipated fluxes and concentrations that can be anticipated in an ecological monitoring situation. The approach selected was primarily dictated by the available data. Both systems yield information on the rate of change in concentration and chemical flux. This information is beneficial when setting sampling frequency requirements. The projections made here suggest very slow rates of change, relatively low concentrations, and relatively low fluxes. Real time monitoring will be difficult due to the low mass and volume flux rates anticipated. Using the results and selecting appropriate instrumentation will increase the probability of a successfully implemented ecological monitoring system. It is critically important to measure or obtain reliable estimates of the flux to adequately evaluate the ecosystem risk or ecosystem monitoring requirements.

ACKNOWLEDGEMENTS

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Monitoring Enhanced *In Situ* Bioremediation in a Fractured Basalt Aquifer

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ABSTRACT: An enhanced *in situ* bioremediation field evaluation was conducted in a deep, fractured basalt aquifer located at the Test Area North (TAN) facility at the Idaho National Engineering and Environmental Laboratory (INEEL). The field evaluation demonstrated that reductive dechlorination of trichloroethene (TCE) can be significantly enhanced by the addition of an electron donor, lactate. Analytes collected during the short-term field evaluation were similar to those recommended in three relevant protocols. The data collected provided an opportunity to evaluate the utility of many of the parameters and the methods used to analyse them. As a result of the extensive monitoring which was conducted during this field evaluation, an abbreviated long-term monitoring strategy has been developed and will be implemented for continued monitoring of enhanced *in situ* bioremediation at TAN.

KEYWORDS: trichloroethene, anaerobic reductive dechlorination, biodegradation, monitoring, bioremediation, chlorinated solvents

INTRODUCTION

The ubiquitous presence of chlorinated solvent contamination in groundwater has led to research of degradation pathways (Vogel *et al.* 1987), and natural attenuation in subsurface environments (EPA 1996). Chlorinated solvents have been shown to be susceptible to anaerobic reductive dechlorination (ARD) both intrinsically and through the addition of electron donor (e.g., EPA 1996, Freedman and Gossett 1989). Monitoring of *in situ* ARD is discussed in at least three technical protocols: the Reductive Anaerobic Biological In Situ Treatment Technology (RABITT) protocol (Morse *et al.* 1998), the Air Force Center for Environmental Excellence (AFCEE) Technical Protocol (Wiedemeier *et al.* 1997), and the EPA Technical Protocol for Evaluating Natural Attenuation of Chlorinated Solvents in Groundwater (EPA 1998).

An enhanced *in situ* bioremediation field evaluation was conducted in a deep, fractured basalt aquifer located at the TAN facility at the INEEL. The TAN facility is the site of a nearly 3-km long TCE plume resulting from the injection of liquid waste directly into the fractured basalt of the Snake River Plain Aquifer during the 1960s. Co-disposed organic materials provided an electron donor to drive limited intrinsic reductive dechlorination in the vicinity of the former injection well. A field evaluation of enhanced *in situ* bioremediation (ISB) was performed at TAN beginning in January 1999. The overall objective of the enhanced ISB field evaluation was to determine whether the biodegradation of TCE through ARD could be enhanced through addition of an electron donor. A major goal of the field evaluation was to monitor the process extensively for the analytes recommended in the relevant protocols and determine the most cost-effective approaches to both short and long-term monitoring.

METHODS

Operations

The ISB field evaluation system design consisted of a 150-m long treatment cell created by an injection well (TSF-05), an extraction well, and eleven monitoring locations. Sodium lactate was regularly pulsed into the treatment cell through the injection well. The extracted water was treated by an air stripper and reinjected downgradient of the treatment cell. Sampling and analysis were performed for all eleven monitoring locations.

Monitoring

Monitoring was conducted at eleven locations throughout the eight-month field evaluation. The monitoring network included seven sampling locations on the axis of the treatment cell, one cross-gradient well, one upgradient well, and two wells located near the plume boundary (see Fig. 1). Eight of the monitoring locations were sampled biweekly, and the remaining three were sampled monthly.

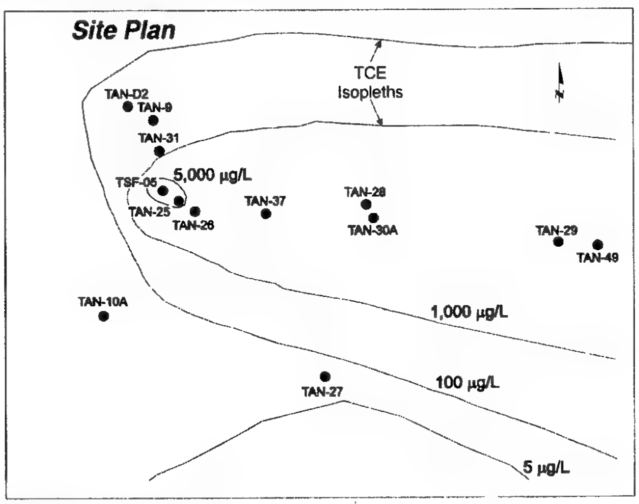

Fig. 1. Site plan and monitoring locations

All wells were sampled using dedicated variable speed submersible pumps. Sampling was performed consistent with low-flow sampling principles (Sorenson *et al.* submitted). In the worst case, drawdown was equivalent to only approximately 0.06% of the 63-m saturated thickness of the aquifer.

Analytes collected during the short-term field evaluation were similar to those recommended in the relevant protocols. These included parameters to monitor electron donor and nutrient distribution, redox-sensitive parameters, chloroethene contaminants and degradation products, biological activity indicators, and water quality parameters. The analytes monitored to track electron donor and nutrient distribution were chemical oxygen demand (COD), lactate, acetate/propionate/butyrate, ammonia, and phosphate. The redox-sensitive parameters, which were measured to monitor competing terminal electron accepting processes (TEAPs), included dissolved oxygen (DO), ferrous iron, nitrate, sulfate, and methane. The chloroethene contaminants and degradation products that were monitored were perchloroethene (PCE), TCE, cis-1,2-dichloroethene (cis-DCE), trans-1,2-dichloroethene (trans-DCE), vinyl chloride (VC), ethene, ethane, and chloride. Alkalinity and carbon dioxide were analysed as indicators of biological activity. The water quality parameters measured were temperature, pH, specific conductance, and oxidation-reduction potential (ORP).

Many constraints had to be considered in developing a monitoring program which would encompass the above parameters. Among these were a limited sampling and analysis budget, limited ability to handle large volumes of hazardous purge water and other wastes, the need to provide data of sufficient quality to satisfy both technical and regulatory requirements, and a tight schedule driven by regulatory milestones. In order to satisfy the field evaluation technical objectives subject to the constraints mentioned, a four tiered monitoring strategy was employed which used a combination of fixed laboratory and field analyses. This strategy allowed the opportunity to evaluate potential surrogates for more expensive analyses.

The first component of the monitoring program was on-site field test kit analyses. These were conducted in an on-site field laboratory using titrimetric and colorimetric field test kit methods and included COD, ammonia, phosphate, ferrous iron, nitrate, sulfate, chloride, alkalinity, and carbon dioxide. Specifics of the field test kits were given in Sorenson *et al.* (submitted). The second component of the monitoring program was continuous *in situ* monitoring for temperature, DO, pH, specific conductance, and ORP. The *in situ* monitoring was conducted at several locations near the injection well using submersible water quality instruments.

A third component of the monitoring program was biweekly fixed laboratory analysis for chloroethenes (PCE, TCE, cis/trans-DCE, VC), ethene/ethane/methane, lactate, and acetate/propionate/butyrate. The chloroethene analyses were performed as a headspace analysis using solid phase micro-extraction (SPME) to sample the headspace and a gas chromatograph (GC) equipped with a flame ionization detector (FID) to analyze the samples. Ethene/ethane/methane and acetate/propionate/butyrate analyses were also performed using a GC/FID. Lactate samples were analyzed using ion chromatography. Full details of the fixed laboratory analytical methods can be found in Sorenson *et al.* (submitted).

The final component of the monitoring program was quarterly split samples sent to off-site laboratories. Samples for chloroethenes, ethene/ethane/methane, and anions (nitrate, phosphate, sulfate, and chloride) were analyzed at off-site laboratories using EPA approved methods in order to provide independent verification of the on-site data. The chloroethene samples were analyzed using EPA Method 8260, the ethene/ethane/methane samples were analyzed using EPA Method 8015M/3810, and the anions were analyzed following EPA Method 300.

RESULTS

Electron Donor

As mentioned earlier, samples were collected and analyzed for both COD and lactate and its degradation products. Figure 2 depicts the electron donor both as the sum of lactate, acetate, propionate, and butyrate (measured individually) and as COD for Wells TAN-25 and TAN-31. The response of electron donor concentrations at Well TAN-25 to the initial lactate addition was essentially instantaneous. Concentrations in the thousands of milligrams per litre were observed in the first sampling event following lactate injection. The COD and electron donor concentrations in Well TAN-25 continued to increase through August, approximately 235 days after the initial injection. Very little electron donor reached Well TAN-31 until the injection strategy was changed on 2 March and again on 9 June, approximately 56 and 155 days after the initial injection, respectively. This change corresponds to an increase in electron donor from 11 mg L^{-1} on 1 March to 181 mg L^{-1} on 21 June (from 6 mg L^{-1} to 241 mg L^{-1} as COD).

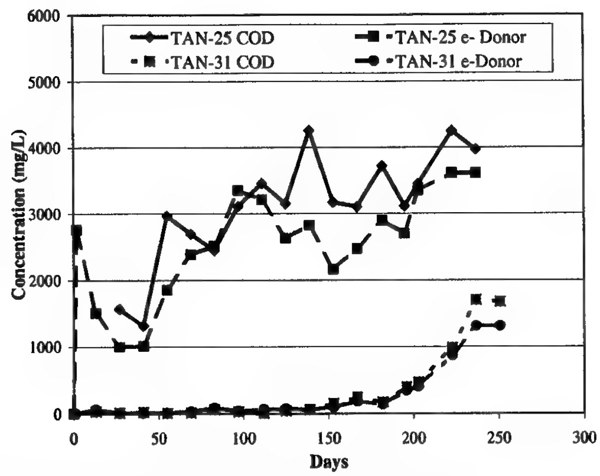

Fig. 2. Electron donor concentrations at Wells TAN-25 and TAN-31

Redox Indicators

The redox conditions were successfully manipulated through electron donor addition as illustrated in Fig. 3 for Well TAN-31. Nitrate concentrations dropped below the method detection limit by the first sampling event following lactate injection. Significant decreases in sulfate concentrations and small increases in iron-II (reduced from iron-III) concentrations were observed at the first sampling event after the lactate injection volume was increased (by decreasing the concentration) on 2 March. The effect of electron donor addition strategy on redox conditions is even more apparent following another injection volume increase on 9 June. In less than four weeks the methane concentrations increased by more than a factor of 5 and continued to increase dramatically.

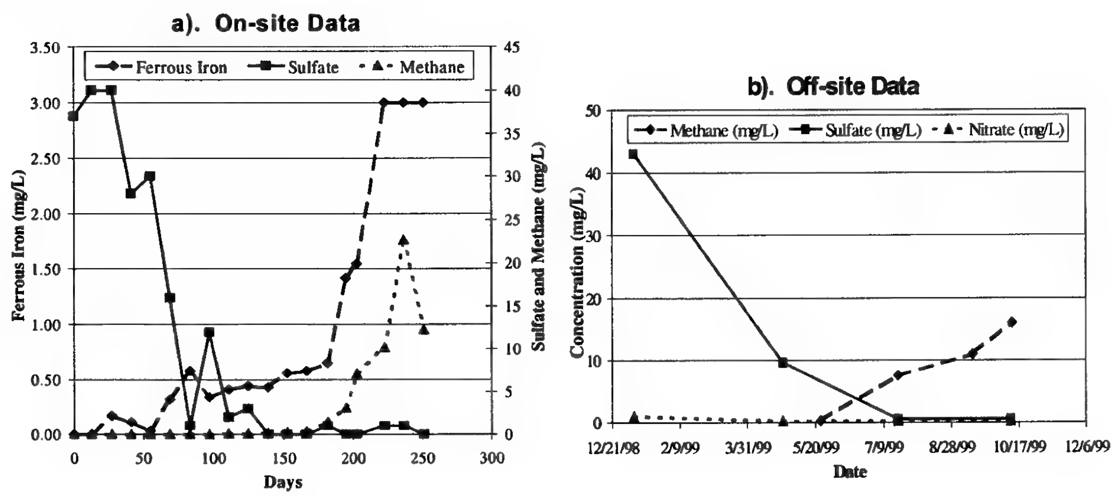

Fig.3. Redox conditions from on-site (a) and off-site (b) analyses at Well TAN-31

Off-site methane, sulfate, and nitrate results for Well TAN-31 were compared to field test kit results to verify the observed redox trends from on-site analyses. Figure 3 illustrates that the off-site data showed the same response to lactate injection at Well TAN-31 as observed through on-site analyses. Both sulfate and nitrate concentrations decreased in Well TAN-31 after lactate addition began (7 January). By July methane was observed in both on-site and off-site samples from Well TAN-31.

Chloroethenes

Dechlorination results are presented in detail elsewhere (Sorenson *et al.*, submitted, Sorenson *et al.*, 2000). In brief, ARD of TCE to cis-DCE occurred less than six weeks from the initial lactate injection in Well TAN-25. Transformation of the cis-DCE to less chlorinated compounds did not occur until late April in Well TAN-25. In general, transformation of TCE to cis-DCE followed the onset of sulfate reduction, and further transformation to VC and ethene followed the onset of methanogenesis. Accumulation of VC was not observed.

Biological Indicators

Figure 4 presents the effects of lactate addition on the biological activity indicators at Wells TAN-25 and TAN-31. The baseline carbon dioxide concentrations averaged 37 mg L^{-1} and alkalinity averaged 160 mg L^{-1}. Both the carbon dioxide and alkalinity concentrations increased significantly from their baseline concentrations.

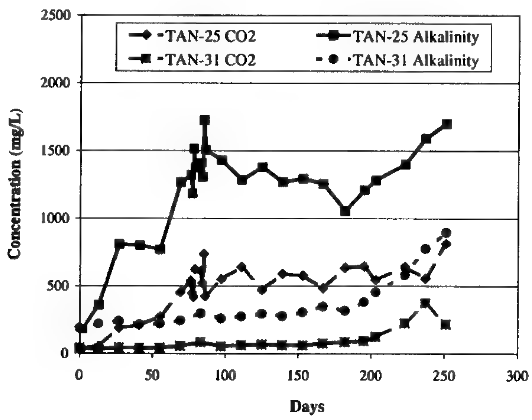

Fig. 4. Biological indicators at Wells TAN-25 and TAN-31

In Situ Monitoring

In situ measurements from Well TAN-37 were collected at four-hourly intervals in order to record changes in response to lactate injections. Figure 5 shows the decrease in redox potential and increase in specific conductance associated with each lactate injection. It can also be seen from Fig. 5 that the travel time of lactate (from Well TSF-05 to Well TAN-37) is approximately seven days.

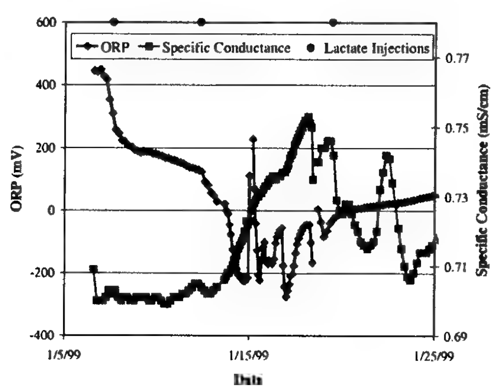

Fig. 5. *In situ* hydrolab data from Well TAN-37

DISCUSSION

The monitoring program from the TAN field evaluation was compared to the RABITT, AFCEE, and EPA protocols for monitoring ARD. The AFCEE and EPA protocols are essentially the same in their recommendations for monitoring. The monitoring program for the TAN field evaluation was consistent with the protocols with a few exceptions.

(a) All three protocols recommend monitoring dissolved organic carbon (DOC), hydrogen sulfide, and nitrite, which were not included in the TAN program.
(b) The EPA and AFCEE protocols recommend monitoring hydrogen and manganese, which were not included in the TAN program.
(c) The TAN program included ammonia and COD, which were not explicitly recommended in any of the protocols.
(d) The TAN program included carbon dioxide, which was not explicitly recommended in the RABITT protocol.
(e) The TAN program included phosphate, which was not explicitly recommended in the AFCEE and EPA protocols.

In general, the EPA and AFCEE protocols recommend either field test kit or fixed laboratory methods for many of the parameters while the RABITT protocol recommends fixed laboratory EPA methods for most of the analytes. The TAN field evaluation was consistent with the EPA and AFCEE protocols' recommendation of field test kits for many analytes and with the RABITT protocol's suggestion of using GC/FID for chloroethenes, ethene/ethane/methane, and volatile fatty acid analyses rather than the EPA methods. The use of these analyses in place of more expensive EPA methods allowed for extensive monitoring to be conducted during the field evaluation at a relatively low cost.

It can be seen from Fig. 2 that COD provides a good qualitative surrogate for the electron donor concentrations. During a short-term field evaluation it is important to understand the fermentation pathways, and therefore more comprehensive analyses should be considered. However, because COD appeared to be such an excellent indicator of electron donor distribution, it could be used in place of lactate and its degradation products for long-term monitoring.

The field test kit analysis of nitrate, sulfate, and ferrous iron, and the GC/FID analysis of methane proved to be sufficient in monitoring the redox conditions at TAN. The off-site analyses for both the anions and ethene/ethane/methane splits generally confirmed the accuracy of individual on-site analyses and have clearly shown the same overall trends. The field evaluation at TAN revealed that sulfate and methane were the key redox-sensitive parameters with respect to dechlorination at the site (Sorenson *et al.* submitted). Comparison of chloroethene data with the redox data revealed that the delay in the conversion from cis-DCE to VC in Well TAN-25 was probably related to the time required for the onset of methanogenic conditions rather than to degradation kinetics. In fact, the generation of VC and ethene in Well TAN-25 corresponds exactly to the onset of methanogenesis. For long-term operations, sulfate and methane appear to be sufficient to monitor redox conditions at TAN.

Analyses for chloroethenes and degradation products provided useful data throughout the short-term field evaluation. The only exception to the utility of these analyses at TAN was chloride. High background concentrations at TAN made detection of any chloride produced by dechlorination nearly impossible.

The primary indicators of biological activity measured during the field evaluation were carbon dioxide and alkalinity. Carbon dioxide is produced from the fermentation of lactate. At pH values less than or equal to 8.3 the carbon dioxide exists as carbon dioxide and/or

bicarbonate, which contributes to alkalinity. Thus, both of these will typically increase with an increase in biological activity. However, the average relative percent difference calculated for duplicates during the field evaluation was much less for the alkalinity analysis. Therefore, the TAN data support the selection of alkalinity and omission of carbon dioxide for long-term monitoring of biological activity.

As illustrated in Fig. 5 the *in situ* monitoring equipment proved to be an inexpensive source of very high resolution data for monitoring redox conditions and electron donor distribution. ORP and specific conductance were effective for indicating a change of conditions in response to lactate injection. Specific conductance increased as sodium lactate dissociated in solution and redox potential decreased as competing electron acceptors were depleted. The *in situ* measurement of ORP indicates when conditions are progressing toward those optimal for reductive dechlorination (~ -400 mV). The continuous *in situ* monitoring may also indicate if or when a system upset has occurred and therefore should be included for long-term monitoring.

Analytes monitored during the short-term field evaluation were similar to those recommended in the three protocols. It was found that several of the analytes recommended in the protocols could be omitted from the field evaluation monitoring program or replaced with a less expensive analysis without losing meaningful data. For example, DOC was not included in the sampling program at TAN because COD provided similar information on electron donor distribution and was obtained using a field test kit. Hydrogen sulfide, nitrite, hydrogen, and manganese were not included in the TAN program because sufficient information regarding redox conditions and active electron accepting processes was gained from the other redox-sensitive parameters (DO, nitrate, ferrous iron, sulfate, and methane).

The protocols provide little guidance for long-term monitoring of ARD as the selected remedial technology. This seems to indicate that the same comprehensive analyte list used for the short-term field evaluation should be used for long-term monitoring. The results of the field evaluation at TAN clearly show that this need not be the case. Based on the results of an extensively monitored field evaluation, an abbreviated analyte list for long-term monitoring can likely be created. At TAN the abbreviated list includes one analyte for electron donor (COD), three redox-sensitive parameters (DO, sulfate, and methane), the chloroethene contaminants and degradation products (PCE, TCE, cis/trans-DCE, VC, ethene, and ethane), and the water quality parameters (ORP, pH, temperature, and specific conductance). Of the nine analyses required to monitor for the above analytes, only two will be fixed laboratory analyses (chloroethenes and ethene/ethane/methane) and the remaining seven will be conducted in the field. Of course, the analytes selected for the long-term monitoring program will be dependent on site-specific conditions, and the long-term monitoring program developed for TAN may not be appropriate at other sites.

CONCLUSIONS

The monitoring program for the short-term field evaluation at TAN was compared and contrasted to the monitoring specified in three protocols for monitoring ARD. The program included most of the same analytes identified in the technical protocols but employed a combination of field and fixed laboratory analyses rather than exclusively using more expensive EPA methods. This monitoring strategy allowed for near real-time data collection and analysis required to optimise electron donor injection strategies during the short-term field evaluation. In addition, the independent off-site analyses verified the appropriateness of the on-site analytical methods. The field evaluation demonstrated that some analytes specified in the protocols could be omitted and that equivalent data for others could be obtained using less expensive, nearly real-time field methods.

The field evaluation also provided an opportunity to compare short-term monitoring needs to long-term monitoring needs. During the initial short-term field evaluation, it is necessary to determine the dependence of ARD on electron donor fermentation pathways and TEAPs, which requires a fairly extensive suite of analytes. Once this is established, a less comprehensive monitoring program than those given in the protocols may be appropriate for long-term operations. Based on the short-term field evaluation results, an abbreviated list of analytes has been identified for long-term operations at TAN.

ACKNOWLEDGMENTS

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Environmental Site Assessment and the Cone Penetrometer Technology

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ABSTRACT: The contamination of various environmental media, (e.g. groundwater and soil) and their potential risks to human health and environment is a serious, complex problem. Site characterisation plays an important role in delineating the extent of the contamination and determining the type of remediation techniques that will be used to clean up a site. A cost-effective, efficiently-designed and well-implemented environmental remediation program is heavily dependent upon the accurate delineation of the areal and vertical distribution of contamination. The cone penetrometer (CPT) is used to gather continuous hydrogeological data in a timely and cost-effective manner. The cone penetrometer can be equipped with a fuel fluorescence detector (FFD) that determines the vertical extent of contamination as the CPT advances into the ground. A comprehensive graphical model of the contamination distribution can be produced allowing the project manager to make field decisions in real-time. This results in a rapid, cost-effective and highly accurate site characterisation.

KEYWORDS: characterisation, cone penetrometer, rapid, delineation, optic fibre, 3D model

INTRODUCTION

An accurate site characterisation is considered one of the most important parts of determining contaminant mass, location, pathways, and consequently determining a technically applicable and cost-effective remedial action. Environmental site characterisation is a relatively new field in Australia. Site characterisation can be a costly and time-consuming process. The initial remedial investigation stage consists of gathering hydrogeological data upon which an effective remedial solution can be derived. This is sometimes found to be the most costly part of the cleanup process because multiple site visits are often required to complete a site characterisation. Traditional boring and drilling techniques are used in Australia to accurately delineate the extent and severity of the contamination and develop a three-dimensional map of the contaminated area. The CPT/FFD represents a significant improvement in site characterisation technology over traditional methods such as conventional drilling. This type of site characterisation technique is faster, more accurate, less expensive, and reduces the workers potential exposure to hazardous materials. The major advantage of this site characterisation technique is the accurate *in situ* determination of contamination concentrations in real-time. This article discusses the environmental applications of the CPT/FFD technology.

Handex has performed over 100 CPT/FFD surveys, allowing Handex's clients to adopt a more timely and cost-effective remedial solution.

CONE PENETROMETER TECHNOLOGY

The cone penetrometer is a truck-mounted, direct push platform for deploying geotechnical and advanced environmental sensors into the ground. Data is acquired *in situ*

and transmitted to an on-board computer for analysis. The result is rapid, cost-effective method for developing highly detailed stratigraphic profiles and determining vertical and lateral distribution of hydrocarbons in the subsurface. Soil, groundwater and soil gas samples can also be efficiently collected rounding out the capabilities of the cone penetrometer. The CPT permits the collection of samples and data from multiple test points in a single day.

Cone Penetrometer Capabilities

The cone penetrometer has been used successfully for half a century for conventional geotechnical exploration applications. The CPT is ideal for environmental site characterisation because it is a direct push method that produces no drilling spoil and therefore does not present the waste disposal problem inherent in traditional drilling and sampling.

Site stratigraphy

A continuous stratigraphic profile is automatically developed as the cone penetrometer is advanced into the ground. Tip resistance and sleeve friction measurement collected by the piezocone are used to develop a stratigraphic profile. Figure 1 shows a graphical representation of the CPT probe. Standard soil classification, density and hydraulic conductivity are some of the characteristics that can be obtained during a standard site characterisation exercise. Pore pressure is also measured by the piezocone when it enters a water-containing horizon using a porous media and pressure transducer. The cone penetrometer is stopped after it enters the water-containing horizon to allow for pore pressure to dissipate and preventing the cone movement from increasing the pore pressure. The data collected provides information about the vertical distribution of both perched and confined groundwater horizons.

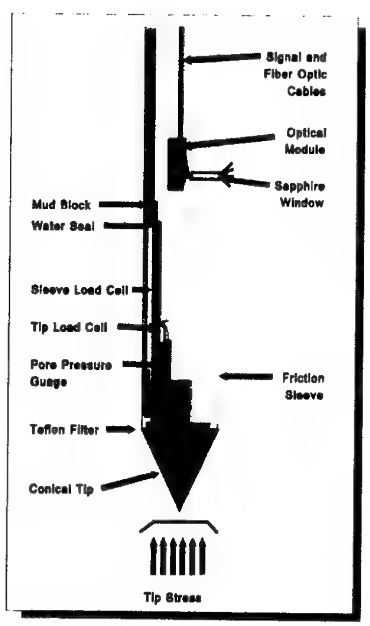

Fig. 1. CPT Probe provides continuous stratigraphic and hydrocarbon measurement as the probe is advance into the ground

Fuel fluorescence detector

The cone penetrometer can also be equipped with a fuel fluorescence detector (FFD) to determine the vertical distribution of hydrocarbons. Hydrocarbons fluoresce when they are exposed to ultraviolet light. The FFD uses this property to measure the hydrocarbon concentration in the soil. The FFD module, mounted directly behind the piezometer, projects ultraviolet light through a sapphire window onto the adjacent soil. The ultraviolet light is absorbed by hydrocarbons which become fluorescent. The emitted energy is reflected back through the sapphire window and transmitted to the surface through a fibre optic cable. The optical signal is converted into an electrical signal using a photomultiplier, and then is communicated to an acquisition computer. The data output is expressed as fluorescence intensity as a function of depth. The intensity of the fluorescence is proportional to the concentration of hydrocarbons in the soil. This hydrocarbon detection method does not require the collection of a soil sample and constant screening of the samples with a PID. The cone penetrometer is not equipped to collect soil samples, however it determines the exact location where samples should be collected, minimising the collection of unnecessary samples. Figure 2 shows an example of a boring log automatically produced by the on-board computer. The key advantage of this type of approach is the ability to provide real-time information concerning the location of the contaminate plume above and below the water table.

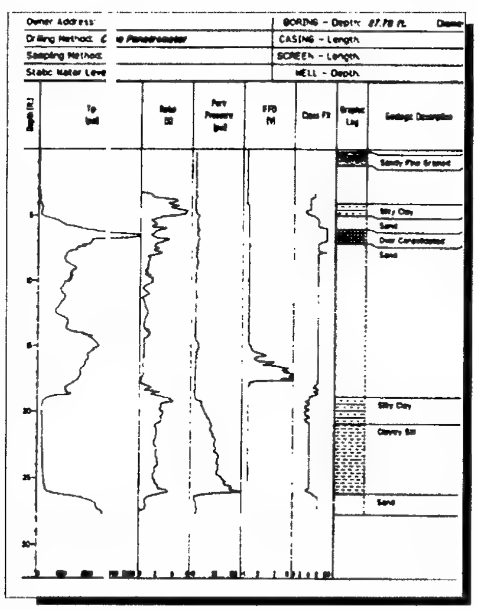

Fig. 2. Tip, pore and FFD pressure measurement provides detailed subsurface information necessary to develop an effective remedial plan

Computer modelling

Rapid site characterisation and visualisation of the information collected by the CPT is achieved by importing the CPT/FFD data into modelling programs such as three dimensional stratigraphy models, and geological cross sections. Iso-concentration maps are one of the most important modelling programs used to graphically represent the contaminant distribution in the subsurface. This data provides a comprehensive snapshot of the subsurface, helping the decision maker quantify the impacted media in real-time allowing for a more accurate site characterisation, reduced cost and allows for a more accurate assessment of the potential risk

to sensitive receptors given the location of the impacted media. Figure 3 shows an example of a 3-D plume model.

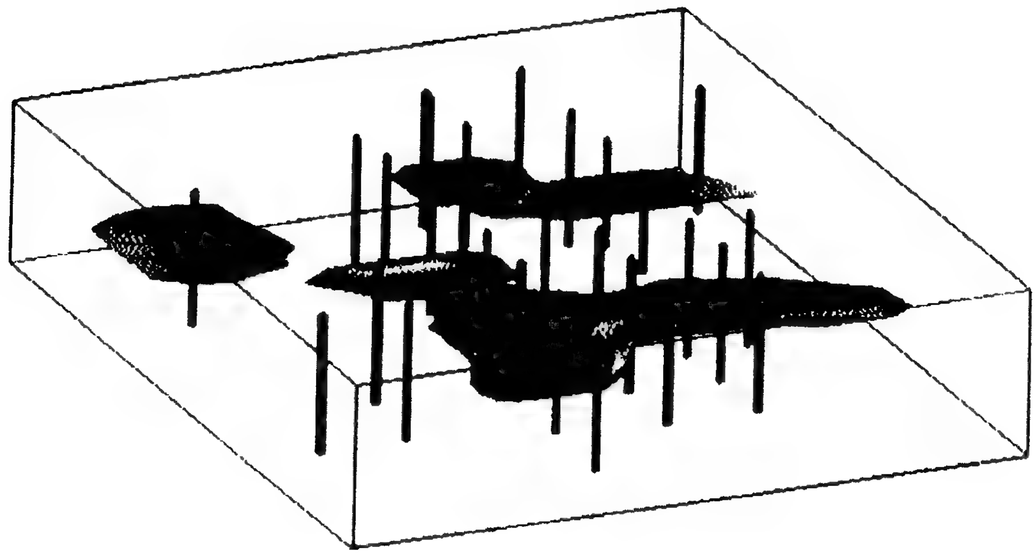

Fig. 3. Computer visualisation provides a snapshot of the subsurface so that decision maker can understand and quantify risk associated with soil and groundwater contamination while still in the field

Groundwater sampling

Groundwater samples can be collected during standard piezocone penetration without physically retracting the probe. This is possible by using a multi-level groundwater sampling tool called "conesipper" that is mounted directly behind the standard FFD unit. The conesipper is decontaminated down hole and then advanced to the next sampling depth as the piezometer data is being collected. Small diameter wells can be installed using the cone penetrometer.

PROJECT PROFILE - CASE STUDY

A large chemical manufacturer commissioned Handex to operate and maintain an existing treatment system. The system was put in place by another consultant who discovered and attempted to delineate a toluene plume. Handex reviewed the system data and discovered that it was not effectively recovering toluene, prolonging remediation time and therefore increasing running costs. Handex felt that the toluene plume has not been completely delineated. The use of the cone penetrometer in conjunction with the FFD was recommended to properly delineate the toluene plume.

Scope of Works

The scope of works consisted of:

(a) installation of sixteen CPT/FFD soundings to a depth of 6.0m below ground level;
(b) collection of soil samples to correlate FFD signal;
(c) installation of three temporary groundwater monitoring wells to measure separate phase toluene;

(d) collection of a product samples to confirm product identity;
(e) development three iso-concentration maps of the CPT/FFD data collected during the investigation to visualise the location and extend of the toluene plume.

Outcomes

The CPT/FFD investigation determined there was a small quantity of toluene remaining in the vicinity of the installed recovery wells. The plume of separated phase toluene was discovered in an area of the site which was not previous suspected as a source. The source of the contamination was found to be a 50-mm toluene distribution line removed several years ago. The data collected during this CPT/FFD investigation was used to redesign the remediation system and suggest several cost reducing options for our client's consideration. The suggested options helped to decrease the duration of the system operation and ultimately save the client over $150000.

SUMMARY

The CPT/FFD unit offers several advantages over conventional drilling techniques in the delineation and understanding of contamination problems. The CPT provides rapid, cost-effective and accurate delineation of contamination by using a range of cone attachments allowing it to measure relevant physical, chemical and geological conditions. The direct data import into multiple modelling programs for characterisation and subsequent interpretation in real-time is considered one of the most significant improvements in site characterisation.

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Ceramic Dosimeters for Time-Integrated Contaminant Monitoring

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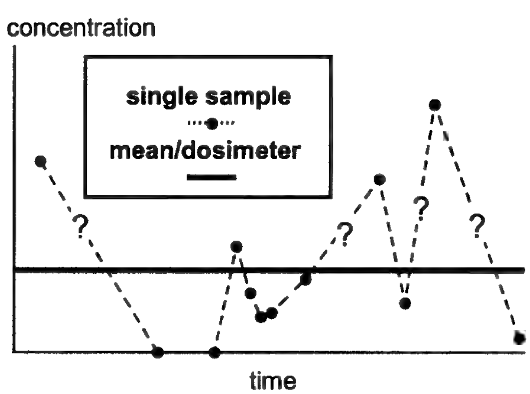
ABSTRACT: Sampling with ceramic dosimeters (passive samplers, patent pending) is a new method which was developed for long-term, time-integrated monitoring of organic pollutants in groundwater and surface water. Artifacts which are common for other water sampling methods (e.g. during transportation, storage etc.) are avoided with this new sampling method and the number of necessary analyses is reduced to only a few while monitoring the contaminant concentrations (representative mean values) over the whole sampling period. This concept of time-integrated concentration measurements can be used equally for contaminant monitoring in groundwater as well as in rivers, lakes, wastewater etc. The method has so far been developed and tested for polycyclic aromatic hydrocarbons (PAH), volatile chlorinated hydrocarbons and volatile aromatic compounds (BTEX), but can also be used for other organic and inorganic aqueous contaminants.

KEYWORDS: dosimeter, passive samplers, time-integrated sampling, long-term contaminant monitoring, groundwater, surface water

INTRODUCTION

The common sampling methods (e.g. pumped water samples) only detect the momentary concentration of contaminants in groundwater and surface water. In order to evaluate the contaminant concentration over a longer time period, all the variations have to be measured and their average must be found (Fig. 1). When taking only a few water samples over a long time period the values detected might only be short-term extreme values (too high or too low), which would then lead to significant interpretation errors. In addition to this,



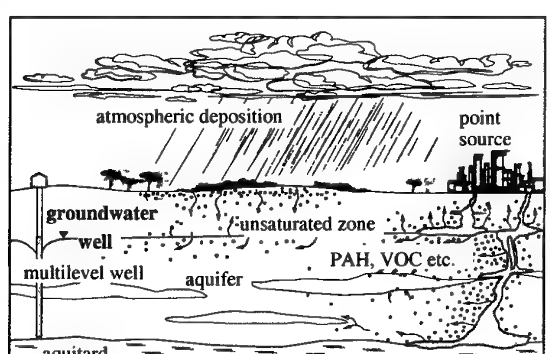


Fig. 1. General scheme of the time-integrating sampling concept with a dosimeter (passive sampler)

groundwater sampling with pumps leads to a change in the hydraulic flow field, which could cause a dilution of the contaminants. For highly volatile compounds such as BTEX evaporation during the sampling procedure may lead to lower values in the water samples.

The main advantage of the new method presented in this paper is the time-integrated monitoring during the whole sampling period (possibly many months). This reduces the number of required analyses to only a few, avoids sources of error during sampling, transportation or storage of a water sample and reduces the costs.

The time-integrated monitoring of organic contaminant concentrations e.g. in groundwater is achieved by using dosimeters that are installed in sampling wells and continuously accumulate contaminants from the contact water onto a suitable adsorbent material. A ceramic membrane is used for the control of diffusive fluxes and this allows the calibration of the system.

Other researchers proposed passive samplers for the monitoring of surface water (DiGiano *et al.* 1988, Hofelt and Shea 1997). For example Lebo *et al.* (1995) used polyethylene membranes with triolein as adsorbent material. Gale (1998) developed a model describing the contaminant accumulation for this type of passive sampler. Mehltretter and Sorge (1995) proposed passive samplers for soil air monitoring. A system of multi-level sampling for ionic compounds in groundwater is already commercially available (Lobbe Inc.). In contrast to the ceramic dosimeter presented in this paper, all these methods rely on the equilibration of the aqueous concentration with the adsorbent material and therefore do not allow the time-integrated monitoring of contaminant concentrations over extended periods of time. They can only give information about the momentary contaminant concentration, whereas the new system (Grathwohl and Schiedek 1997, Martin *et al.* 2000a,b) determines the long-term average concentration.

METHODS

Dosimeter Design

Dosimeters can be built according to different designs, e.g. using a water-saturated or a dry adsorbent bed. In both cases the contaminants accumulate by diffusing from the contact water through a membrane into the adsorbent bed. They accumulate with time, depending on the concentration gradient and the effective mass transfer coefficient across the membrane (diffusion coefficient/diffusion distance; see Figs 2 and 3). The most promising flux controlling membranes are porous ceramic materials that are commercially available as discs or cylinders of different thicknesses, pore sizes and porosities. These ceramic membranes allow high diffusive fluxes of the solute due to the high porosities. If necessary they can be effectively impermeable to water due to very small pore sizes. A further advantage is that they are practically inert and do not accumulate organic solutes (which would lead to a time-lag in solute uptake in the adsorbent bed). For the long-term operation of either the dry or water-saturated dosimeter, it is important to use an adsorbent material with a high sorption capacity, in order to keep the concentration gradient at a maximum during the whole monitoring period (thus guaranteeing linear uptake).

Suitable adsorbents for organic compounds such as polycyclic aromatic hydrocarbons are ion-exchange resins (e.g. IRA-Amberlite®). They are easily wetted by water and show high accumulation factors as well as high recovery rates for hydrophobic organic compounds. For quantitative analysis, the adsorbent is solvent-extracted after the desired sampling period. For volatile chlorinated hydrocarbons and BTEX, Tenax is a suitable adsorbent. In this case, the adsorbent is thermally desorbed and therefore should be dry. This is achieved by the use of

ceramic tubes with very small pore sizes. The average contaminant concentration in the water, which has been in contact with the dosimeter can be calculated from the accumulated mass of contaminants during the sampling period.

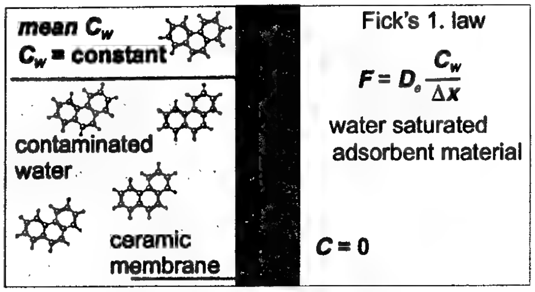


Fig. 2. Concentration profile and fluxes in a dosimeter with adsorbent material (pre-saturated with clean water). D_e denotes the effective diffusion coefficient in the porous ceramic membrane, t the contact time and C_W the (mean) contaminant concentration in contact water. F and Δx are the diffusive flux through the ceramic membrane and the diffusion distance (thickness of the membrane), respectively. The organic compound shown is phenanthrene.

During the monitoring period the contaminant diffusion rate through the membrane occurs at steady state and therefore is solely controlled by the water saturated membrane of thickness Δx (Fick's first law). The cumulative mass, M, which has diffused through the membrane into the adsorbent bed can be calculated by Eqn (1):

$$M = F \cdot A \cdot t = D_e \cdot \frac{\Delta C}{\Delta x} \cdot A \cdot t \qquad (1)$$

where F, A, t, D_e denote the mass flux through the ceramic membrane [M t^{-1} L^{-2}], the membrane surface area [L^2], the sampling time [t] and the effective diffusion coefficient, which is given by: $D_e = D_W \cdot \varepsilon^m$; where D_W, ε and m denote the diffusion coefficient in water [L^2 t^{-1}], the porosity of the ceramic material and Archie's law exponent (approximately 2, (Martin 2000) obtained by the calibration), respectively. $\Delta C/\Delta x$ is the concentration gradient across the membrane.

If a dosimeter with dry adsorbent material is used, the contaminants (e.g. phenanthrene, BTEX or volatile chlorinated hydrocarbons) first have to diffuse through the water saturated ceramic membrane and then through an air film into the adsorbent bed (Fig. 3).

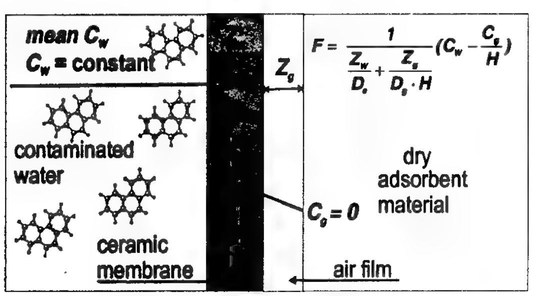


Fig. 3. Double film diffusion model for the flux of contaminants from water into a dosimeter with dry adsorbent material. C_w denotes the concentration in water. C_g, the concentration in air next to the adsorbent material, which is kept close to zero. Z_w is the thickness of the water film and Z_g is the thickness of the air film.

The steady state flux into the dosimeter is given by the double film diffusion model which leads to Eqn (2):

$$F = \frac{1}{\frac{Z_W}{D_e} + \frac{Z_g}{D_g H}} (C_W - \frac{C_g}{H}) \qquad (2)$$

where D_g, C_w, C_g, H denote the diffusion coefficient in air [L^2 t^{-1}], the concentration in water, and the concentration in air next in the adsorbent bed [M L^{-3}] and Henry's law constant ($H = C_g/C_w$), respectively. Z_w and Z_g are the thicknesses of the water film [L] and the air film [L] (e.g. the effective distance between the adsorbent material and the ceramic membrane).

For the operation of either the dry or water-saturated dosimeter it is important to use an adsorbent material with a high sorption capacity. This keeps the concentration gradient at a maximum during the whole sampling period (thus guaranteeing linear uptake). In the ideal case the accumulation of contaminants in the adsorbent material can be described with a partitioning coefficient, K_P, independent of the concentration:

$$K_p = C_s/C_w \tag{3}$$

where C_S and C_w denote the adsorbed and aqueous concentrations. Usually K_P increases with decreasing water solubility of the compound.

RESULTS

Results from the calibration of the dosimeter as well as from field application are shown in Figs 5 - 8. In field and laboratory tests, this method showed very good reproducibility and a linear solute uptake over an extended period of time. Also demonstrated was the ability of the ceramic dosimeter to keep a sorbed contaminant and, therefore, to detect even short-term events in long-term monitoring periods. The collected contaminants do not significantly desorb and diffuse out of the adsorbent bed back into the water when the concentration in the water declines.

Calibration

In order to check the performance of the dosimeter in laboratory experiments, dosimeters were exposed to a saturated solution of phenanthrene in water for different periods of time, varying from two to more than 70 days. To prevent water flowing into the ceramic tubes during immersion the ceramic tubes were closed with a silicone plug at each end after being filled with adsorbent material. To ensure that the concentration of phenanthrene remained constant (solubility concentration) throughout the experimental period, excess phenanthrene was added to the aqueous solution, thereby providing an *in situ* reservoir of organic contaminant. After the dosimeters were removed from the contaminated water, phenanthrene was extracted with suitable solvents such as acetone. The concentrations in the extracts were quantified based on internal standards and GC-MS analysis. The solute masses recovered from the water saturated adsorbent material of the dosimeters are presented in Fig. 5 as a function of time of exposure of the dosimeter to the contaminated water. Samples were taken in triplicate to check reproducibility.

Due to the higher solubility and volatility of toluene a more sophisticated experimental setup was used for the calibration of the ceramic dosimeters with dry adsorbent material (Tenax). Water was spiked with a stock solution in a mixing chamber using a syringe pump and pumped through a column containing the ceramic dosimeters. The water concentration was checked each day and normalised to the standardised value. The solute masses recovered from the ceramic dosimeters with dry adsorbent material using thermo-desorption are presented in Fig. 6 as a function of the time of exposure (up to 30 days). In general, very good reproducibility and linearity is reached.

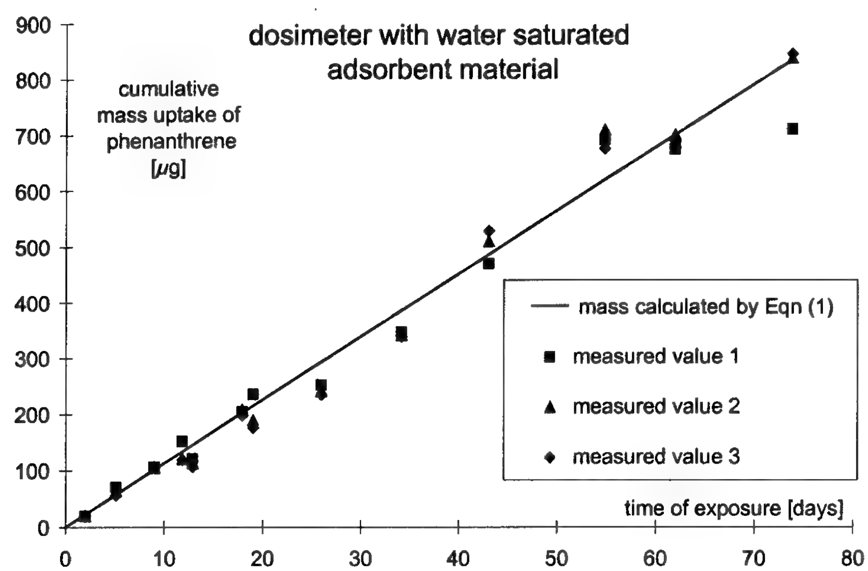


Fig. 5. Linear uptake of phenanthrene in a porous ceramic tube with water saturated adsorbent material (10 cm length, 100 nm pore size) measured over more than 70 days. The solid line represents the calculated/calibrated cumulative uptake following Eqn (1) ($\varepsilon = 31.9\%$; $m = 1.7$; $D_e = 1.12 \times 10^{-6}$ cm^2 s^{-1}; $\Delta C = 1.2$ µg cm^{-3}; $\Delta x = 0.15$ cm; $A = 17$ cm^2) (Martin *et al.* 1999).

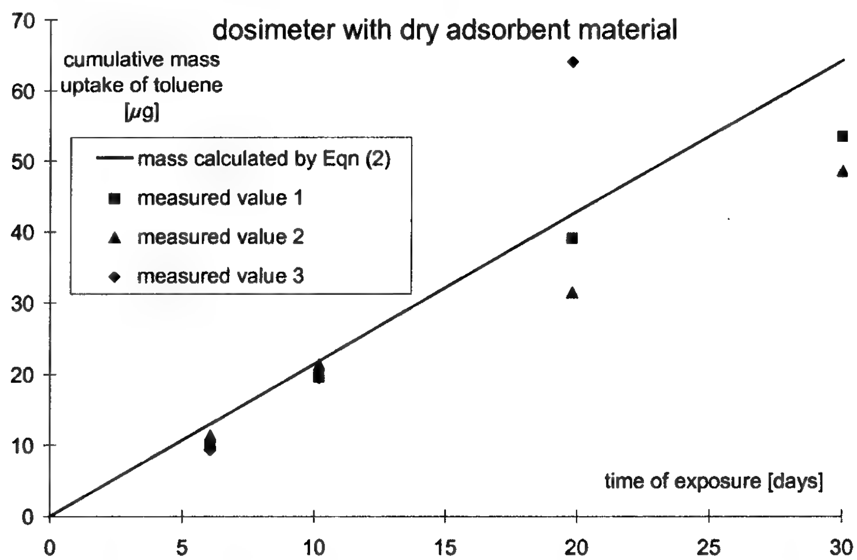


Fig. 6. Linear uptake of toluene in a porous ceramic tube with dry adsorbent material (5 cm length, 5 nm pore size) measured over 30 days. The solid line represents the calculated/calibrated cumulative uptake following Eqn (2) ($\varepsilon = 30.5\%$; $m = 2$; $D_e = 8.90 \times 10^{-7}$ cm^2 s^{-1}; $\Delta C = 0.1$ µg cm^{-3}; $Z_W = 0.03$ cm; $Z_g = 0.1$ cm; $D_g = 7.81 \times 10^{-2}$ cm^2 s^{-1}; $H = 0.21$; $A = 8.35$ cm^2).

Memory And Long-Term Stability

A further advantage of the ceramic dosimeters is that once collected, contaminants do not significantly desorb and diffuse out of the adsorbent bed back into the water when the

concentration in the water declines. In order to validate this, loaded dosimeters (i.e., containing a specified contaminant concentration) were immersed into clean water for different periods of time, up to almost 100 days. The concentration of the contaminant found within the dosimeters after this period was compared with the initial concentration.

In detail, twelve dosimeters were exposed for about two weeks to a saturated solution of phenanthrene in water, after which the contaminant concentration of three of them was measured using the procedure described above and the remaining nine dosimeters were immersed for the different periods of time in clean water. The recovered masses from this experiment (Fig. 7) showed no decline with time. Thus no desorption occurs from contaminated dosimeters which are exposed to water of lower or zero contaminant concentration. This shows that the sorption capacity is sufficiently high to keep the contaminants (as shown for phenanthrene) in the dosimeter. Therefore the ceramic dosimeters are able to detect short-term high concentrations even in a long-term monitoring period. The results also prove that no losses e.g. due to degradation of phenanthrene in the dosimeter occur even over extended periods of time.

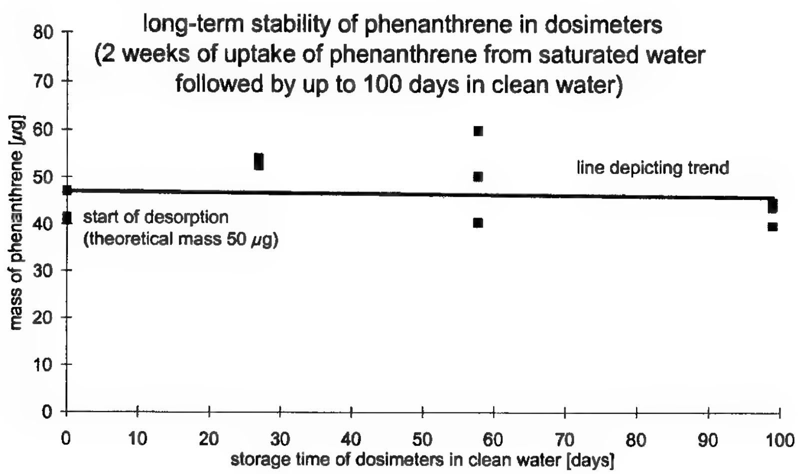


Fig. 7. Tests of the long-term stability of compounds in ceramic dosimeters (5 cm length, 5 nm pore size) over extended periods of time

Similar investigations for VOCs showed a relatively fast decrease for DCE and a slower one for TCE. PCE, monochlorobenzene, toluene and p-xylene showed no decrease. That shows that Tenax is a suitable adsorbent material for these compounds, but for highly volatile compounds such as DCE another adsorbent material (i.e. Carbotrap) should be used.

Field Tests In Groundwater

In field tests, seven ceramic dosimeters were placed in a multi-level groundwater well at a former manufactured gas work site in Kehl (Southern Germany) for more than five months. In Fig. 8, the average concentrations calculated from the masses extracted from the ceramic dosimeters are plotted against the concentrations actually measured in multi-level groundwater samples. This plot is linear over a wide range of concentrations, but shows consistently higher concentrations in the water detected with ceramic dosimeters.

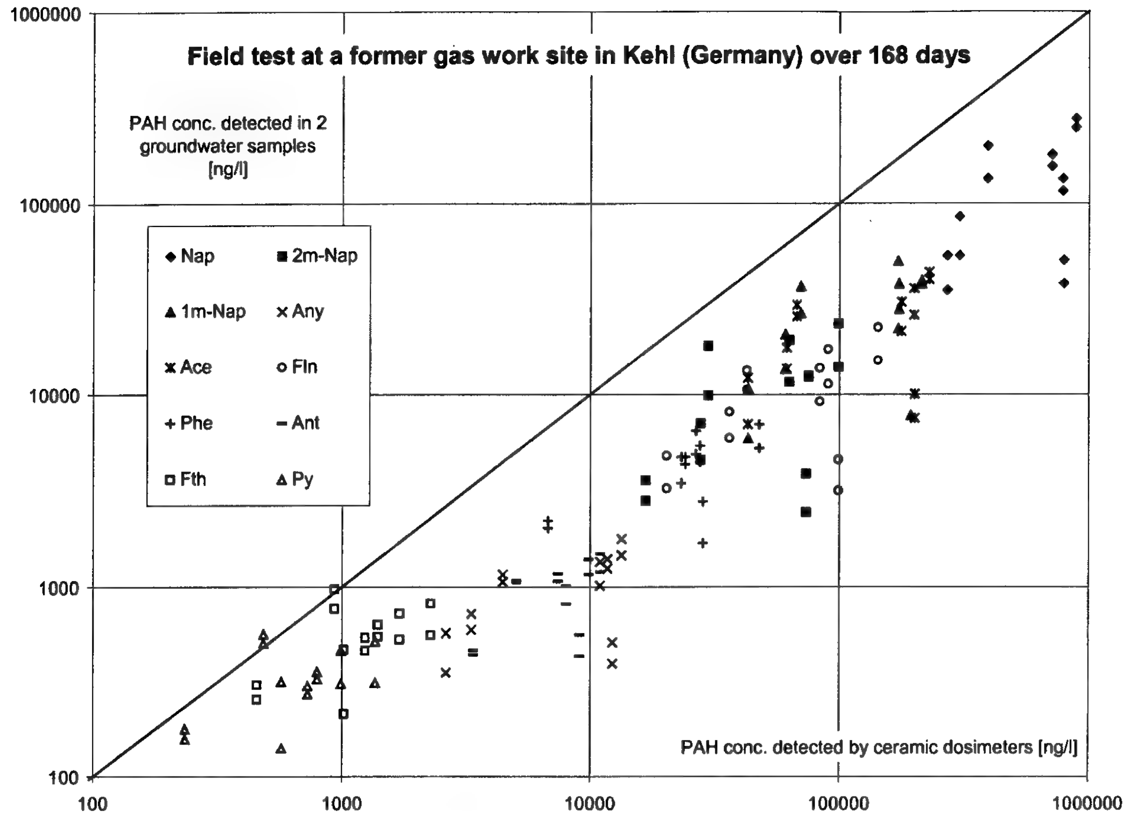


Fig. 8. Comparison of conventional water sampling with ceramic dosimeters in field trials. Ceramic dosimeters were used in a multi-level groundwater well at a former manufactured gas work site in Kehl (Southern Germany) for more than five months.

CONCLUSIONS

The dosimeters show very good reproducibility and a linear solute uptake over an extended period of time (two months of laboratory tests) for the compounds investigated in this study. This emphasises the ability of the ceramic dosimeter to retain sorbed contaminants (see Fig. 7) and therefore to detect even short-term events in long-term monitoring periods. These promising laboratory results were confirmed by field tests at a former manufactured gas work site. The aqueous concentrations obtained in field tests from the dosimeters showed a good correlation to the concentrations measured in pumped groundwater samples. The dosimeter values, however, were significantly higher. This is probably caused by losses due to evaporation, sorption of the solutes in tubing and/or dilution during pumping in conventional sampling.

According to the laboratory and field data, the ceramic dosimeters are suitable devices for monitoring contaminant concentrations over long time periods (many months) in surface water and groundwater.

Further research focuses on field tests over extended periods of time (2-6 months) also for highly volatile contaminants such as chlorinated solvents and BTEX-compounds. Another aim is to further develop the ceramic dosimeters for monitoring of inorganic compounds such as heavy metals or nitrate and use them to monitor natural attenuation processes.

ACKNOWLEDGEMENTS

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Groundwater Flow Tracing by Combined Method of Ground Survey and Measurement in the Boreholes

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ABSTRACT: To identify major flow paths in a shallow groundwater aquifer, a combined tracing method was introduced in a small test field near Tokyo, Japan. As a general survey, temperature was measured 1 m below ground at 28 points (2-m by 1-m grid) in August, September and October 1999. Results from the measurements indicated several flow paths. The triangles of boreholes (W2a, W2b and W2c) were installed along the major flow path and another side normal to it. Through the measurements of groundwater velocity in the boreholes, a major flow path with velocity over 2 mm s^{-1} was found from W2a to W2b. The flow path was also verified by salt water tracing and field pump tests.

KEYWORDS flow path, 1-m-depth ground temperature, measurement in a borehole, CCD camera, salt water tracing

INTRODUCTION

Essential groundwater protection can only be achieved if precise data of actual flow paths and velocities are available. Ground surveys, such as geoelectric and geothermal survey, are suitable for general groundwater systems. However, because of low accuracy, these are not sufficient in estimation of the flow paths. Currently, measurements in the boreholes are a precise method to evaluate groundwater velocity at a point. When we use only the borehole method, however, too many boreholes have to be drilled, making it too expensive and time consuming. Therefore, for the practical reasons, the method combining ground survey and measurement in the boreholes is a more effective.

For a general survey geoelectric methods were popular, however, they require clear access to the sometimes extensive areas being surveyed. In urbanised contaminated areas, open spaces are limited and there are many electric noises to be screened out. Geothermal methods are more effective in shallow aquifer systems in urbanised areas.

Yamada and Ueda (1999) measured groundwater velocities directly in wells and found a zone with high velocity, larger than 1 mm s^{-1}, which was considered to be part of a major flow path. To make sure of identifying the whole flow path, a combined survey method consisted of ground survey and borehole measurements was introduced.

A 1-m-depth ground temperature survey was carried out within an area of 20 m x 5 m by using a 1-m grid in summer, 1999. Low temperature courses reflected flow paths.

Three boreholes (observation wells W2a, W2b and W2c) were installed along the flow path and normal to the path. Direct measurements in the boreholes by CCD camera and water tracing were carried out. The result of these method indicated the same flow path with velocity of 2-3 mm s^{-1}, which coincided with the result from 1-m-depth ground temperature survey.

COMBINED METHOD AND TEST FIELD

The combined method consists of three steps as follows (shown in Fig.1).

Step 1 - General survey to estimate flow path systems.

Step 2 - To install the triangle of boreholes along the major flow path and another normal to it.

Step 3 - To measure velocities in the boreholes by several independent ways.

Yamada and Ishikawa (1994) discussed hydrogeological conditions in the Musashino Diluvial Terrace near Tokyo, where hydraulic conductivities varied widely. In the same field the authors measured velocity in the boreholes by CCD camera.

The small test field is located near the borehole W2 high speed zone with velocity over 1 mm s^{-1} was found by Yamada and Ueda (1999) (shown in Fig. 2).

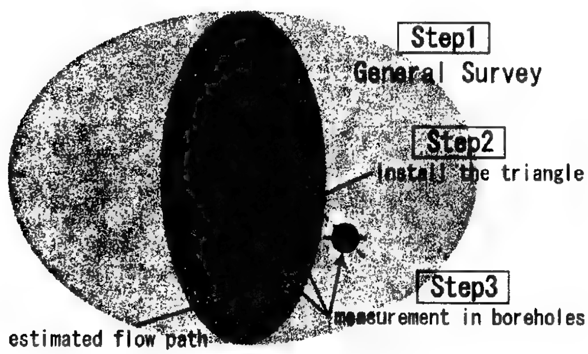

Fig. 1. Combined Method

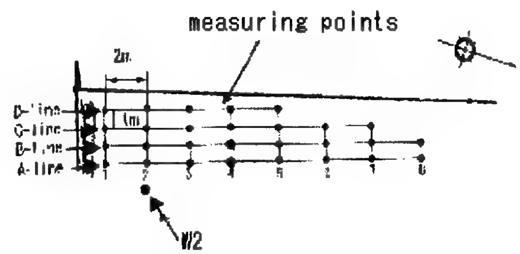

Fig. 2. Test Field and measuring points

1-M-DEPTH GROUND TEMPERATURE SURVEY

Geothermal surveys were used in the area of a thermal spring and landslide. Takeuchi (1980) developed thermodynamic equation for a simple cylindrical flow path and analysed many field data on 1-m-depth ground temperature in mountainous areas. Because of small land slope in diluvial terrace, flow path systems can be more complicated than that in mountainous areas. Therefore, we can only use the geothermal method as a general survey. In the test field, annual mean temperature is 15°C and the temperature of groundwater in the flow path varies within a range of ±2°C.

1-m-depth ground temperature without modification by groundwater in a flow path changes in a range of ± 10°C. The maximum differences in temperature between 1 m-depth ground and groundwater in a flow path are caused in late summer and winter.

1 m-depth temperature just above the groundwater flow path decreases in summer and increases in winter. Figure 3 shows the spatial distribution of 1 m-depth temperature at 28 points in the 1 m × 2 m grid. Temperatures were measured in August, September and October 1999. Essentially, these three results indicate the same depression. Although the results are not sufficient for quantitative evaluation, we can estimate the major flow paths as shown in Fig. 3.

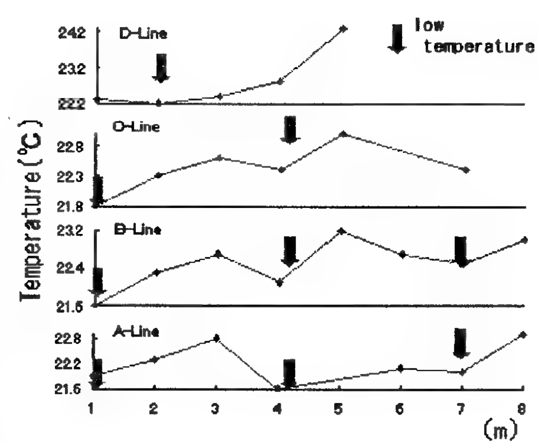

Fig. 3. Results of 1-m-depth temperature survey

THE TRIANGLE OF THE BOREHOLES AND DIRECT MEASUREMENTS BY CCD CAMERA

The triangle of boreholes (W2a, W2b and W2c) should be employed as an effective network to detect the major flow path as shown in Fig. 4. W2a is the centre of the depression, W2b is along the path and W2c is normal to the path. All boreholes have the same inner diameter of 65 mm and length of 15 m with full screen. The area of the screens is open over 30%. One month after drilling, direct measurements by CCD camera (type PZ200, CTIS Co. Ltd.) were carried out in January 2000. In each borehole at 6 or 7 points every 1m-depth velocity was measured by CCD camera. At W2a the results of three tests, as shown in Fig. 5, indicate clear major flow path with velocity over 2 mm s^{-1} and the direction of west at the depth of 10 m to 13 m. Along the flow path, W2b also has a high velocity zone at the depth of 13 m with the same direction of water (shown in Fig. 6). On the other hand, we cannot find any flow path in W2c as shown in Fig. 7.

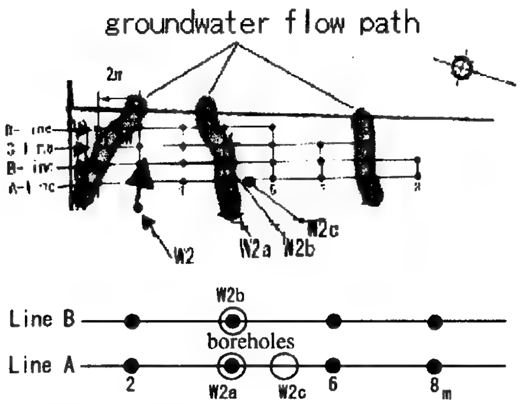

Fig. 4 Groundwater flow path and the triangle of boreholes

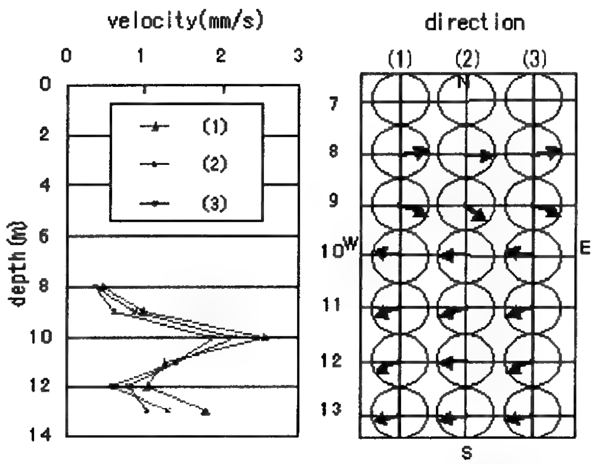

Fig. 5. Velocity and direction by CCD camera

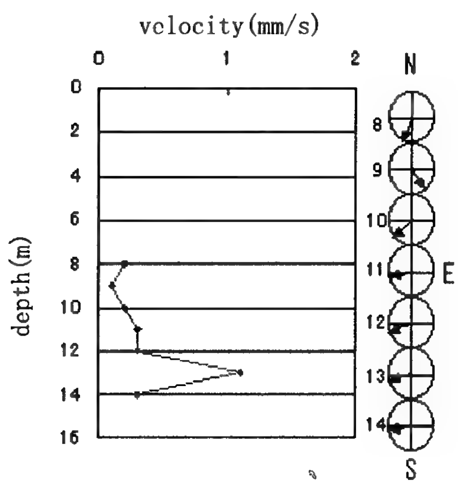

Fig. 6. Velocity and direction by CCD camera

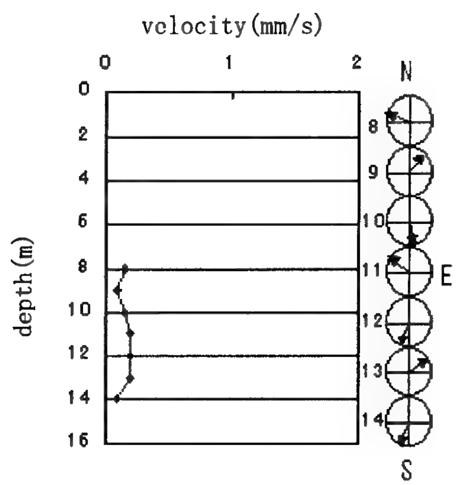

Fig. 7. Velocity and direction by CCD camera (W2c)

SALT WATER TRACING

Salt water with electricial conductivity of 1000 μS cm^{-1} was injected successfully in W2a. At the same time, electric conductivity (EC) in W2b and W2c were measured continuously as shown in Fig. 9. EC at W2b indicates clear change at the time of 300 s after injection. On the other hand at W2c EC is nearly constant during the whole time. From these tracings velocity from W2a to W2b is 3 mm s^{-1}, which coincides with the results from geothermal method and CCD camera method.

We can summarise these results in Fig, 9.

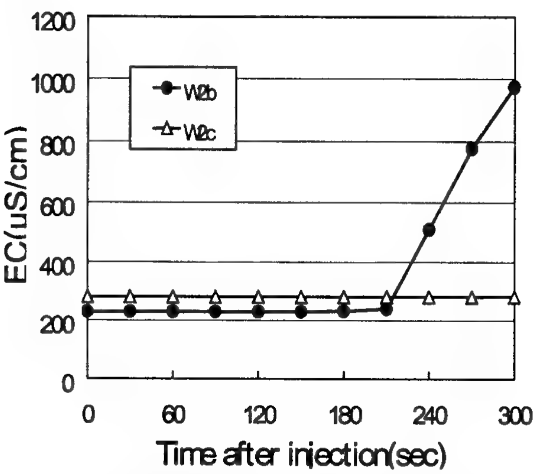

Fig. 8. Change in EC at W2b and W2c (Tracing method)

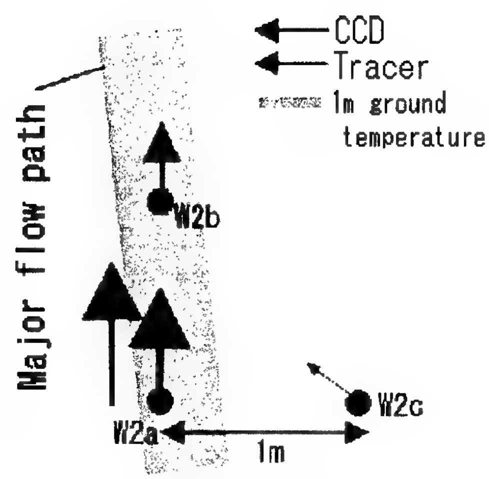

Fig. 9. Summary of the combined method

FIELD PUMP TEST

For the practical purpose, to estimate hydraulic conductivity we sometimes try to pump at the single well. Hydraulic conductivity is given by Borell (1955) as follows

$$Q = \frac{\pi K (h_s^{\,2} - t^2)}{2.3 \log_{10}(R / r_0)} \left\{ \left(0.3 + 10 \frac{r_0}{H} \right) \sin\left(1.8 \frac{h_0 - t}{H} \right) \right\}$$

where K is hydraulic conductivity (cm s^{-1}), Q is discharge of pumping (cm^3 s^{-1}), R is radius of influence (cm), r_0 is inner radius of the well (cm), H is depth of aquifer (cm), h_S is depth from water table to bottom of the well before pumping (cm), h_0 is depth from water table to bottom of aquifer during pumping (cm) and t is depth from water table to bottom of the well during pumping (cm).

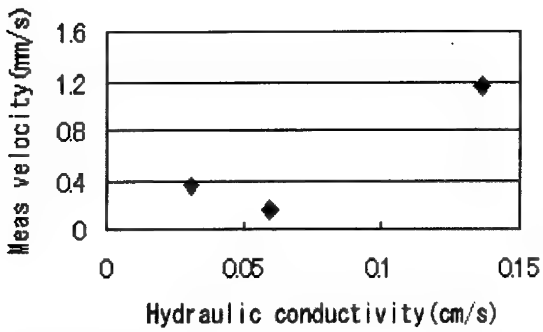

Fig. 10. Relation between mean velocity by CCD camera and hydraulic conductivity

Fig. 10 shows the relation between mean velocity over the depth by CCD camera and hydraulic conductivity by pump test. They have clear regression line, however, according to Darcy's law hydraulic conductivity should be much larger. For quantitative discussion it requires more field measurements, further consideration of basic (maybe non-Darcian) laws for the groundwater movement in a major flow path.

CONCLUSIONS

Estimating the whole system of groundwater flow paths is time consuming and expensive. For practical purposes we introduced a combined method which consisted of general survey and borehole measurements.

In this paper the main conclusions are as follows.

(a) As a general survey, 1-m-depth ground temperature survey was employed and the flow path system was found.

(b) The triangle of the boreholes was installed along the major flow path and normal to it. High velocities (over 2 mm s^{-1}) were measured along the major flow path by CCD camera.

(c) Salt water tracing at the boreholes indicated the flow path with velocity of 3 mm s^{-1}.

(d) Hydraulic conductivity was estimated by field pump test and had a relation to mean velocity by CCD camera.

(e) From the measurements at 1 m×1 m triangle of boreholes, diameter of the flow path is smaller than 1 m.

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Use of Geostatistics in the Assessment of Sites with Complex Contamination Patterns

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ABSTRACT: Statistical data assessment is becoming increasingly popular with assessors of contaminated land. Most statistical approaches are generally based on classical single variable theory. While these classical techniques are usually adequate for relatively simple contamination problems or smaller sites, they tend to break down on complex sites or are inefficient on large site assessments. This paper discusses some of the pitfalls and inefficiencies of the uni-variate approach and outlines an alternative method using bi-variate geostatistical methods. Bi-variate statistics allows simultaneous analysis of two variables, such as concentration and distance between samples. The method essentially relates concentration to sample distance by use of a variogram. Results of the variogram are then used to interpret concentration distribution using Kriging. Kriging offers several significant advantages over classical techniques by allowing assessment of the spatial relationship between concentrations at sample locations in two or three dimensions and predicting the confidence in the interpretation of the data. Kriging not only considers distance between concentration measurements, but has the facility to make allowance for geological features, groundwater flow direction and physical constraints on the data set. Case studies, which compare the classical approach with the Kriging method, are presented, to highlight the benefits of the bi-variate approaches.

KEYWORDS: statistics, bi-variate, geostatistics, kriging, site assessment, data interpretation

INTRODUCTION

Contaminated land assessment professionals have used classical uni-variate statistical methods as a tool for data interpretation for more than a decade. In New South Wales (NSW), publication in 1995 of the NSW EPA "*Sampling Design Guidelines*", provided the first officially endorsed statistical data assessment methodologies. These guidelines outline a number of statistical methods that can be utilised to develop sampling plans and analyse laboratory data. A number of the techniques published in the NSW EPA document are also contained in the Standards Australia (AS 4482.1-1997) "*Guide to the sampling and investigation of potentially contaminated soil. Part 1: Non-volatile and semi-volatile compounds*".

Both documents rely on uni-variate statistics and generally consider concentration only. Uni-variate statistics rely purely on the population distribution of the variable. The normal and log normal distribution are the most commonly used population distribution patterns (Harr 1987), and both are utilised in the NSW EPA and Standards Australia publications. Harr (1987) also outlines other concepts for modelling population distribution, based on uni-variate statistics.

While the uni-variate statistical approach may work for relatively straightforward contaminated sites, with simple geology and contaminant distribution, the approach breaks down on larger sites that may have a complex geology or contaminant distribution pattern.

The bi-variate statistical approach for assessment of concentration data was developed in the 1960s for use in the minerals exploration industry (Krige 1981). This approach examines concentrations in relation to their spatial distribution. Until recent years this approach has not been used by contaminated land assessors, mainly due to the large number of complex calculations required. Since fast personal computers and appropriate software have become commonly available, the bi-variate statistical approach has become an economical alternative to the uni-variate data analysis methods.

This paper discusses the benefits offered by the bi-variate (geostatistical) approach over the traditional methods and presents some examples where bi-variate statistics have been applied.

GEOSTATISTICS FUNDAMENTALS

In contrast to traditional statistical methods, geostatistics does not assume that the samples are random and independent. The theory of geostatistics is well documented in the literature (Royle 1980, Rendu 1981, Krige 1981).

Variograms

The variogram (Fig. 1) is the basic tool of geostatistics (Royle 1980) and expresses the spatial correlation between adjoining samples. A variogram is constructed by calculating the mean squared difference between sample values over incremental sample spacings.

Methodologies for calculation of the mean squared difference and construction of variograms are outlined by a number of authors (Royle 1980, Henley 1981, Rendu 1981, Krige 1981, Ferguson 1992, Marquis and Smith 1994) and are therefore not outlined here.

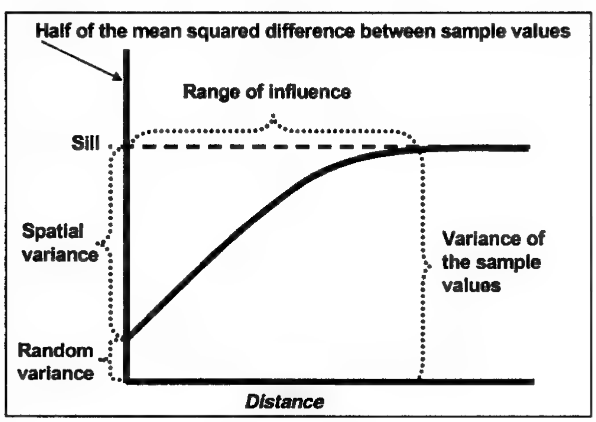

Fig. 1. Features of a variogram

Variograms present a number of key geostatistical properties, which are shown on Fig. 1. The range of influence is the distance over which the sample values are related. Total variance of the samples can be split into a random and spatial component. Random variance is also referred to as the nugget effect.

Kriging

The variogram information is used to krige the data. Kriging is a data interpolation technique that utilises the range and variance values presented on a variogram to carry out a linear moving average estimation of concentrations over a defined area. Again the theory and methodologies for kriging are documented by a number of authors (Rendu 1981, Krige 1981).

BENEFITS OF GEOSTATISTICS

The major benefits offered by the geostatistical approach are (Royle 1980):
(a) provides a rational theoretical basis for intuitive data interpretation;
(b) recognises that total variation contains a random and spatial component;
(c) removes biases of traditional types of estimators;
(d) provides a better estimate of the extent and volume of contaminated media;
(e) provides a confidence measure in any interpretation;
(f) provides estimation of extent and volume that is free of biases; and
(g) provides useful check on sampling effectiveness.

In contrast, uni-variate statistics do not recognise spatial variation and therefore attribute all variance to randomness. This shortcoming limits the applicability of the uni-variate statistical method.

APPLICATION OF GEOSTATISTICS

The following case studies illustrate the use of uni- and bi-variate statistics. In the first case a hypothetical database is used to illustrate random and directional contamination, while the others utilise actual data from recently assessed industrial sites.

Case Study 1

In this case, a hypothetical 1-ha facility comprising a centrally located manufacturing building and two large above ground storage tanks in the northeast and southwest corners (Fig. 2A) was assessed. Site historical information indicates that both tanks contained toluene and were connected to the building by underground pipes. The site was also filled over time using excavated materials from a number of unknown sources.

The NSW EPA sampling design guidelines recommend that 21 samples be collected on a grid pattern to allow detection of a 25.7-m diameter hot spot, with a 95% confidence. Sample locations for this type of assessment are shown on Fig. 2A. Using a geostatistical approach, five targeted locations along the underground pipeline and five random locations across the remainder of the site were selected to characterise contaminant levels in the soils. These sample locations are also shown on Fig. 2A. To demonstrate random contamination, lead concentration (Table 1) in the fill is used, while toluene (Table 2) is used to demonstrate directional contamination.

Assessment of lead contamination

Table 1 indicates good correlation between the two sampling approaches for the lead results, with the only notable difference being the mean. The five random sample mean was higher than the 21 grid sample mean. By comparison to the full data set, the 21 grid sampling

approach better estimates the mean concentration than the five random targetted samples, while both methods provide good estimates of the actual standard deviation. Therefore, from the contaminant concentration perspective, the grided approach appears to be better at estimating the mean than the geostatistical approach adopted for this example. A larger number of random samples is likely to overcome this.

The next step in the geostatistical approach was to assess the spatial relationship between the samples by plotting a variogram. Figure 2 (B) presents the variogram for the lead concentration distribution on the site and showed that the total variance was comprised entirely of the random component, with no apparent spatial relationship. Following analysis of the variogram information a confidence plot was developed for both approaches using kriging.

Table 1. Comparison of lead data sets collected with NSW EPA and geostatistical approaches

Approach	No Samples	Mean (mg L^{-1})	Min (mg L^{-1})	Max (mg L^{-1})	Standard Deviation
NSW EPA	21	110	1	315	107
Geostatistics	10	153	2	315	108
Actual Data	1000	114	1	512	109

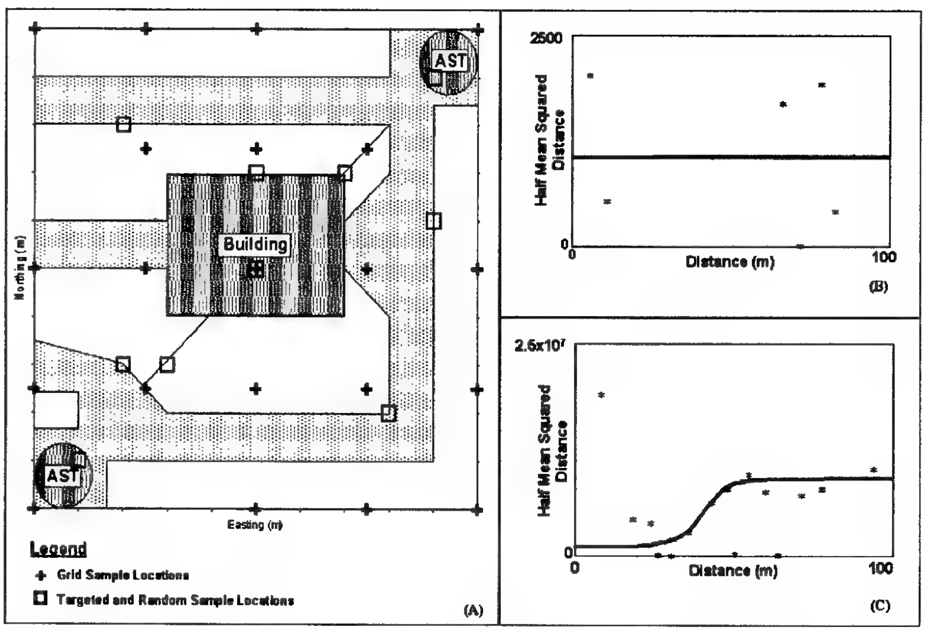

Fig. 2 (A) Plan of the site showing sample locations, (B) Variogram for lead, (C) Variogram for toluene

The confidence plots (Figs 3 (A) and 3 (B)) show that both sampling approaches restrict the 95% confidence limit in the data interpretation to the areas immediately around each sampling point. The geostatistical approach does provide confidence over a larger area than the grided approach and clearly demonstrates that a closely spaced sample grid would be required to achieve 95% confidence across the entire site.

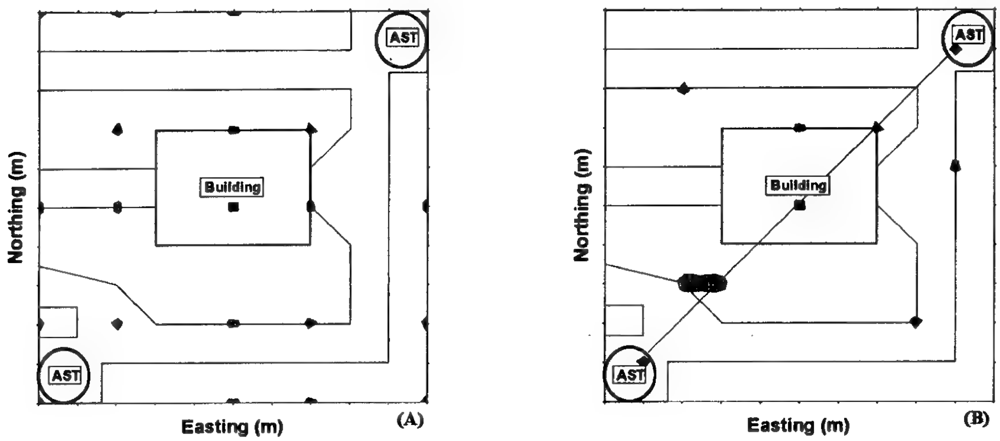

Fig. 3. 95% confidence plots for lead using (A) NSW EPA and (B) Geostatistical approach

Assessment of toluene contamination

Table 2. Comparison of toluene data sets collected with NSW EPA and Geostatistical approaches

Approach	No Samples	Mean (mg L^{-1})	Min (mg L^{-1})	Max (mg L^{-1})	Standard Deviation
NSW EPA	21	365	Not Detected	4582	1115
Geostatistics	10	1385	Not Detected	5820	2001
Actual Data	1000	1953	Not Detected	5820	1850

For the toluene (directional contamination) example, Table 2 clearly demonstrates that the geostatistical approach better estimated the mean and standard deviation of the actual data than the grided approach, using less than half of the samples.

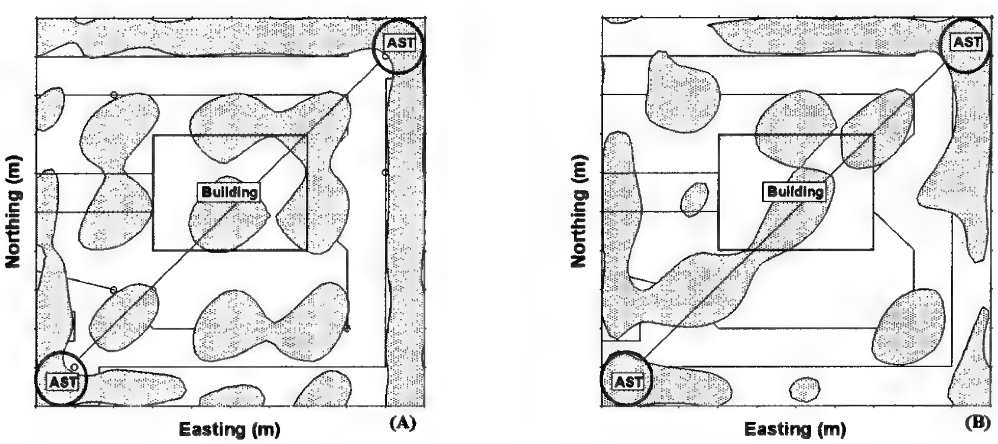

Fig. 4. 95% confidence plots for toluene using (A) NSW EPA and (B) Geostatistical approach

The toluene variogram (Fig. 2 (C)) shows that that there is a good spatial relationship in the data and the confidence plots (Figs 4 (A) and 4 (B)) shows better site coverage along the toluene pipeline.

Case 1 therefore demonstrates that data interpretation ability of both methods is limited for randomly distributed data. The NSW EPA guidelines overcome this by recommending that the grid sampling pattern is designed to detect circular hot spots of a predetermined size. The

geostatistical approach can overcome this by assessing how many samples are required to achieve 95% confidence in the site coverage.

Case Study 2

A geostatistical assessment of groundwater data collected on a former gasworks site was undertaken to establish if a sufficiently dense network of monitoring wells had been established to define cyanide impacts on the groundwater below the site. The aim was to be 95% confident in the data reliability. Due to client confidentiality this site could not be identified.

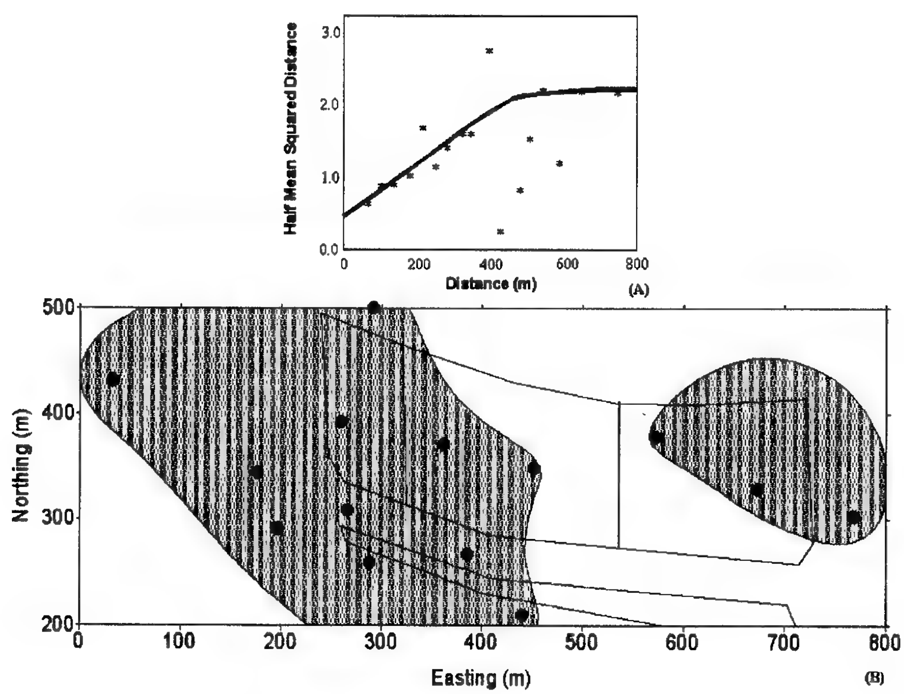

Fig. 5. (A) Variogram and (B) confidence plot (shaded area >95%) of site for case 2

The variogram indicates that spatial variance exists in the cyanide data and a confidence plot could therefore be generated. Based on the confidence plot a sufficient number of wells are present in the western part of the study area to achieve almost total site coverage at a 95% confidence. Some additional monitoring wells would be required in the eastern half of the study area, to achieve coverage at the 95% confidence interval. This could be done in a staged approach by reassessing the data and optimising monitoring well locations at each stage.

Case Study 3

A number of site assessments at a former gasworks facility were undertaken to identify the extent of polycyclic aromatic hydrocarbon (PAH) impact on the fill soils. Due to client confidentiality this site could not be identified. A geostatistical data assessment approach was adopted to assess the clean and contaminated sections of the site at the 95% confidence level. Fig. 6 presents the variogram plotted for the site assessment data.

The variogram (Fig. 6) indicates that a significant portion of the total variance is random and that the range of influence is relatively limited compared to the maximum sample spacing.

Based on the variogram a kriging approach was developed to plot the areas on the site where clean and contaminated conditions were predicted with a 95% confidence. Kriging was also used to plot the areas where soil PAH concentrations exceed the site criteria. Results of the kriging are presented on Fig. 7.

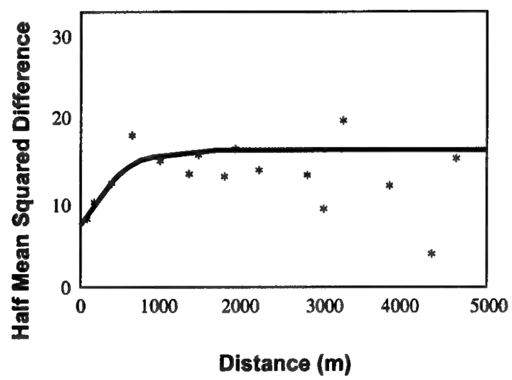

Fig. 6. Variogram of PAH concentration in soil at the former gas works facility

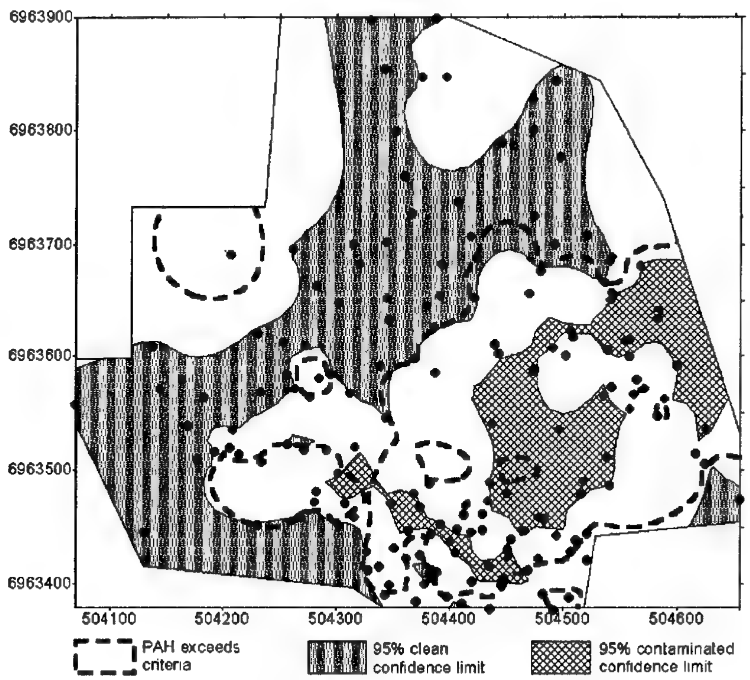

Fig. 7. Plot of 95% confidence intervals and PAH distribution at the former gasworks site

The purpose of the geostatistical analysis was to establish target zones where additional samples would be required to predict the status of the soil at the 95% confidence level and to estimate the soil volume that will require remediation. Figure 7 shows that the area predicted to have soil PAH concentrations above the site criteria, is larger than the area of the 95% confidence limit prediction. This is in part due to the limited number of samples collected in some areas of the site and also the high component of random variance in the data set.

In this case the use of geostatistics has significantly enhanced the site assessment results by identifying key areas where additional data is required and allowing estimation of the likely remediation costs at various confidence intervals.

CONCLUSIONS

Geostatistical data assessment has several distinct advantages over traditional univariate techniques, including:

(a) splitting the variance into a random and spatial component; and
(b) establishing the distance over which samples influence each other.

Although initially developed for use in the mining industry, geostatistics are now being used by assessors of contaminated land, because the method:

(a) provides significantly more information on the reliability of the data set;
(b) acknowledges that a spatial relationship exists between concentration and sample spacing;
(c) is independent of sampling pattern; and
(d) avoids over sampling of sites.

As demonstrated by the case studies, bi-variate geostatistics are a useful tool for assessment of contaminated land and can offer a practical alternative to the methods outlined in the NSW EPA (1995) "Sampling Design Guidelines". Particularly on sites where detailed site historical information is available, geological conditions are defined and contaminant distribution is complex.

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Maximising Data Utility for Contaminated Sediment Management

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ABSTRACT: The assessment and management of risk in contaminated marine sediments is a complicated and often contentious issue. The core, and one of the major costs, of this process is the collection, interpretation and communication of site data. Ultimately, disparate data types, such as standard and innovative chemical and toxicological measurements, benthic community analyses, hydrological and other models must be brought together, synthesised and communicated to a wide variety of stakeholders. Data summaries should be designed, stored and delivered in a form which allows results to be applied to multiple uses – both anticipated and unanticipated. Examples of how information from multiple data sources can be integrated and graphically presented to focus attention on critical sites, rank sites based on multiple parameters, and communicate outcomes of variable management priorities are presented.

KEYWORDS: data communication, sediment management, decisions

INTRODUCTION

Because of past industrial activities, ship activity, non-point source input, etc., sediments at numerous sites have some level of impact from anthropogenic compounds. A recent United States Environmental Protection Agency (USEPA) report (1998) identified 96 watersheds in the United States as having areas of probable concern for sediment contamination. As marine sediment and coastal sites fall under increasing scrutiny, the number of sites for which ecological risk assessment, and potentially, management, will be deemed necessary is bound to increase. Contaminated sediment sites must be ranked and prioritised, and cost-effective management strategies must be developed. It is assumed that the management process will seek to balance two parallel goals: (a) minimising contaminant risk to the environment and human health and (b) minimising cost (NRC 1997).

Marine sediments have a number of features which make them less straightforward to manage than soil sites. Sediments in coastal areas are often integrators of contaminant input from multiple non-point sources within a watershed. This creates difficulties in tracking sources of contamination, and also results in ubiquitous, regional 'background' levels of anthropogenic contaminants which are difficult to separate from site-specific sources. For the same reason, sediments, much more often than soils, are impacted by multiple contaminants of potential concern (COPCs), making risk and management decisions complex. While soils and groundwaters are often geographically removed from the receptors to be protected, sediments are in direct contact with the benthic community, which is near the base of the food chain which requires protection. Sediments are subject to a multitude of regulatory criteria, from local to national and international. According to NRC (1997), 'The mechanisms of the regulatory process in a given situation depend on where the sediments are located; where they will be placed; the nature and extent of the contamination; and whether the purpose of removing or manipulating the sediment is navigation dredging, environmental cleanup, site development or waste management.' As a result, multiple regulators or stakeholders may have different goals, cleanup criteria, or contaminants of concern which drive their part of a site management decision.

The range of sediment management options exist on a continuum – beginning with those requiring no containment or physical control, through more aggressive *in situ* treatment and containment technologies, and finally, ending with removal and disposal or treatment technologies. In essence, in-place sediment management consists of 'pathway interdiction' while ex-situ approaches represent mass removal. If contaminants are to be left in place, it is critical to evaluate potential pathways by which contaminants might pose an ecological or human health risk, and to monitor, minimise or eliminate these pathways, particularly in surface sediments. On the other hand, if sediments are to be removed, it is essential to know more about sediment characteristics as a function of depth (to determine volumes to be removed) and of whole volumes of sediment (to determine treatability or consequences of disturbance or disposal).

Given the economic, logistical, technological and ecological limitations of sediment removal and treatment technologies, it is inevitable that some contaminated sediments will be left in place, in the short or the long term, even if contaminants pose some ecological or human health risk. However, leaving sediments in place has met with regulator and public resistance at many sites due to concerns about the long-term risk to the marine environment. Decisions must be made which minimise uncertainty in a complex, multivariate system; address multiple and often conflicting priorities and agendas; minimise costs; and stand up to public, legal and regulatory scrutiny.

Frequently, original site assessment data are collected without input from the eventual modellers, decision makers, and risk managers on data needs. Since sediments risk assessments are often begun with no clear idea of where along the continuum site management will end, data are often collected iteratively. A minor extra investment to assure that samples and data collected will serve the needs and priorities of multiple users or stakeholders can assure broader utility of data, and help prevent iterative sampling events, thus expediting site decisions at reduced cost. Once collected, it is critical that data are summarised and communicated in a manner which can address the concerns and priorities of all stakeholders who will be part of the decision process.

THE USE OF SEDIMENT CHEMISTRY DATA

A screening risk assessment (SRA) helps to determine whether a potential exposure pathway is present between chemicals of interest and selected ecological receptors and to estimate risks for those chemicals for which pathways are identified. Risks can be estimated by comparing maximum chemical concentrations directly to media-based threshold values, or by modelling chemical doses to ecological receptors and then comparing the dose estimates to threshold dose values. Potentially unacceptable risks are indicated for those chemicals that have environmental concentrations or doses that exceed selected threshold values. These chemicals are termed contaminants of potential concern (COPCs). Once COPCs have been identified, areas within a site or region can be ranked to determine those sites or areas of greatest concern. Areas can also be compared to determine if similar or different 'patterns' of contamination exist – potentially pinpointing various sources of contamination, or sediments which can be managed as a unit.

Areas of concern can be ranked by a number of criteria, depending upon the priorities of the stakeholders and the questions being asked of the samples (which can vary depending upon what part of the decision process is being addressed). As an example of various ways chemical data can be used, data from a site were examined and compared to potential ecological benchmarks.

Site Background

The site to be discussed is the area in and around a lagoon located at the southeastern corner of a naval air station which is slated for closure (see Fig. 1). Beginning in the mid-1980s, studies at the site have resulted in the analysis of a wide variety of sediment samples, for a full suite of potential contaminants, as well as toxicity, sediment geochemistry, and microbiology, among other parameters. Detailed examination of contaminant contours suggested that, while anthropogenic compounds were detected in all the sediments in the lagoon, only sediments from the northwest and northeast corners showed levels which were significantly above threshold levels. The two corners, which were at the mouths of outfalls (no longer in use), showed levels of PAHs, PCBs and some metals which were significantly above regional ambient levels and either effects range-low (ER-L) or effects range-medium (ER-M) levels (Long *et al.* 1995). Because some contaminant levels in these outfall areas were high, the bulk of the regulatory attention has been focused on these regions and the perception of the lagoon itself is driven by the high numbers at the outfalls. This has led to the opinion by some that the entire lagoon should be dredged before the site is closed. The estimated cost for this action is about $100000000. Others suggest that the entire lagoon be transferred without any remedial action because the outfall regions are small compared to the whole lagoon and are not a source of significant exposure. Outside the lagoon area, the major sources of concern were the pier areas, where some PAH and toxicity 'hits' were observed, and the beach area, which may have been impacted by ship and industrial activity.

The data discussed here are from surface grabs from a series of transects designed to delineate extent of contamination around 'hotspots' identified in past studies (the outfall areas in the lagoon, the pier and the beach areas). Reference samples were also collected from five regional sediment sites considered minimally impacted. In data plots, samples L1-L5 represent a transect moving from the northeast corner (outfall) of the lagoon area to the central area (shown in the map in Fig. 1), L6-L11 represents a similar transect from the northwest corner (outfall). Samples B1-B6 represent a northeast-southeast transect of the beach area, P1-P6 represent a northeast-southwest transect of the pier area, and R1-R6 represent the reference samples, not shown. In data plots, field duplicates (i.e., L8 and L11; B3 and B6; P2 and P6; R2 and R6) are plotted next to each other.

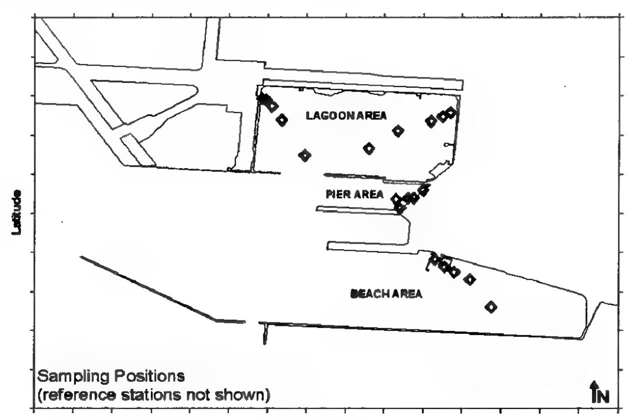

Fig. 1. Sampling map

Chemical Results

When examining bulk chemical concentrations in sediments, it is important to compare them to some criterion or benchmark. However, a choice of appropriate benchmarks is dependent upon a definition of the objectives of the work. If the objective is a determination of the potential risk of a COPC in the sediments, one can compare bulk chemical values to levels which are expected to be toxic in sediments (e.g., ER-L, ER-M). Such values are often termed sediment quality guidelines (SQGs). If the objective is to determine whether, for a given COPC, the sediment being examined differs from other comparable sediments, one can compare bulk chemical values to background, regional or reference values. Often, a combination of the above is useful, so that data may be used in more than one way. In this paper, we compare the data to effects range-low (ER-L, lower 10th percentile of the effects data), effects range-median (ER-M, the 50th percentile of the effects data); from Long *et al.* (1995) and, in some cases for PCBs, a regional ambient value, based upon the 85th percent confidence interval around results from a regional study (Gandesbery and Hetzel 1998).

Figures 2 and 3 show various ways of presenting site chemical data (total PCB, total PAH, Ag, As, Cd, Cr, Pb, Zn and Cu), from PRC (1998), to extract different information from the sites. In Figs 2a,b data are reported as the sums of 'hits' – exceedances of a given SQG (ER-L and ER-M, respectively). Examination of Fig. 2(a) allows for the potential elimination of only small areas of sediment from consideration; all samples had at least one COPC which exceeded ER-L. Many of the samples exceed ER-L for most of the analytes, though the beach area seems decidedly less complex than the pier and lagoon areas. Examination of Fig. 2(b), however, suggests that the areas of greatest concern can be narrowed. Only the samples closest to the outfalls in the lagoon transects and closest to the piers in the pier area exceed ER-M values. Examining which COPCs exceeded ER-M in each sample suggests that the major sources of contamination may differ between areas. Cr is apparent in only one corner of the lagoon, and PAHs are a major contributor in the pier area, but not in the lagoon.

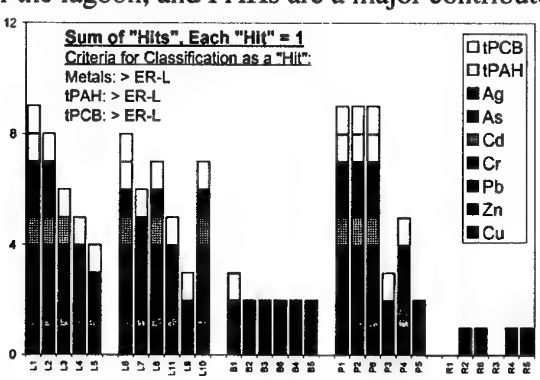

Fig. 2(a) Site ranking using 'hit' summations based upon COPCs exceeding ER-L

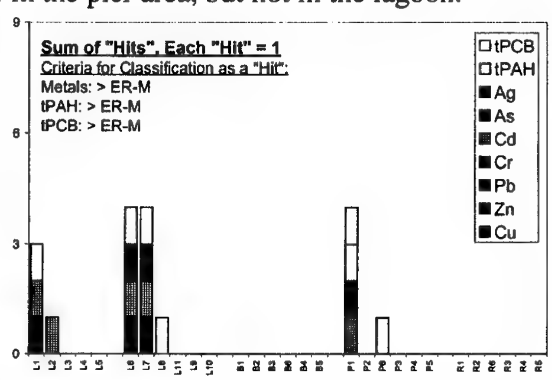

Fig. 2(b) Site ranking 'hit' summations based upon COPCs exceeding ER-M

While the data presentation described above can give an indication of which COPCs exist at a site, it is impossible to address the relative importance of the COPCs to risk at the site. Even a single ppm or ppb exceedance above an SQG has as much weight as an exceedance of several orders of magnitude. In such an approach, a sediment with moderate levels of many contaminants is given more weight than a sediment which is extremely impacted with a single contaminant. Another approach is to define SQGs for each COPC, and then to normalize sediment COPC concentrations to SQGs to determine the relative contribution to potential risk of a given COPC (e.g., Kreis 1989). The resulting COPC-

specific hazard quotients (HQs) account for the degree of exceedance of a given COPC above a benchmark. The COPC-specific HQs can then be added up, to compare samples or sites. It should be pointed out that the selection of contaminant-specific SQGs is not a trivial process, since they are based upon assumption of risk, and risk in itself is a relative term. Generally, it is defined for a given COPC/organism pair as a function of hazard and exposure. Thus, risk depends upon the bioavailability of a COPC to a given organism, which varies as a function of countless field conditions, and the mode of exposure. Generally, different stakeholders are concerned with different receptors – there are ecological, fishery, human health and other concerns. Effective sediment management seeks to address and balance these often competing priorities. Thus, different SQGs can be used to address different goals. One can select to use one type of SQG for all COPCs (e.g., ER-M), or one can select different SQGs for different types of contaminant, depending upon the COPC-specific risk assumptions.

As an example, two potential scenarios are presented below. In the first, all stakeholders are concerned with acute toxicity issues, so all contaminants are normalised to ER-M (Fig. 3(a)). In the second scenario, one stakeholder whose charter it is to protect wildlife is particularly concerned with bioaccumulative contaminants. In the region under discussion, PCBs in fish tissue are high – this stakeholder feels that ER-M (and ER-L) are not protective enough, and feels that sediments should be managed to regional background levels of PCBs, as a minimum. To address this concern, while all other COPCs are normalised to ER-M, PCBs are normalised to a regional reference value (Fig. 3(b)). In this case, since reference values are significantly lower than ER-M values, this has the effect of heavily weighting PCBs in the HQ sum. In both these cases, bulk sediment concentrations of a COPC are divided by a selected SQG, to generate a compound-specific hazard quotient (HQ). Then the HQs are added up for each sample, even if less than one.

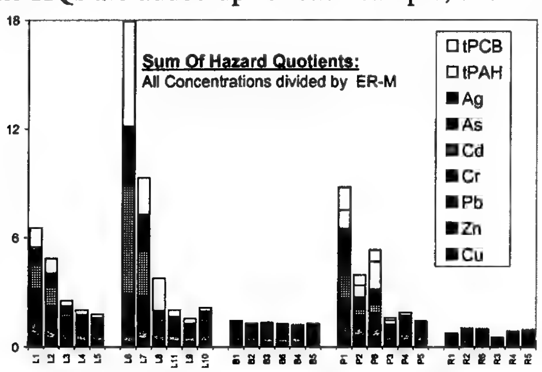

Fig. 3(a) Site ranking using sum of hazard quotients, all COPCs concentrations divided by ER-M

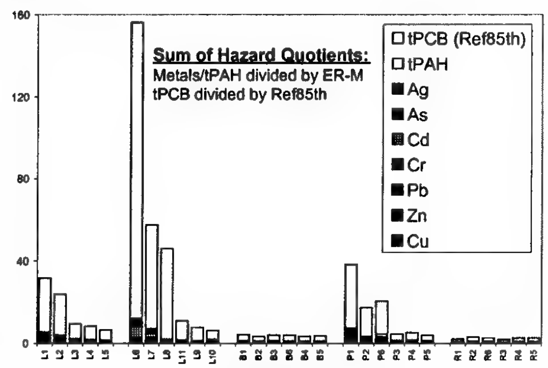

Fig. 3(b) Site ranking using sum of hazard quotients, metals and PAH COPCs concentrations divided by ER-M, +PCB concentrations divided by regional reference levels

The use of HQs clearly makes a difference in the way these sites are ranked. Figure 2 did not allow for the relative ranking of the two outfall areas in the lagoon and the near-pier area. Figure 3(a) suggests that the northwest outfall area is significantly more contaminated than are the other areas. Furthermore, the relative impact of various COPCs becomes apparent. Cd appears to be a major contributor to both the lagoon and pier area sites, as are PCBs and Ag. However, PAHs figure prominently only in the pier sites. While the sum of the hazard quotients in the beach area are, on average, a bit higher than they are in the reference samples, no single contaminant has an HQ>1, suggesting that the difference is minor. HQs drop off dramatically as transects move away from areas of concern in the lagoon and in the pier area. This information suggests that while there are sites of potential concern

in these regions, the worst areas cover relatively small volumes of sediment. It should be pointed out, however, that the HQs for all the lagoon sediments samples are higher than those of the reference sediments, even if individual contaminants do not exceed ER-M in the sediments away from the hotspots. These data can be used to guide a discussion about potential risk management strategies for the sites in question.

If Scenario 2 is examined (Fig. 3(b)) the story is more complex. Dividing tPCB levels by a regional reference value rather than ER-M makes PCBs dominate the HQ sums for all samples. The HQ sums for the beach area samples are now ~2x higher than the reference areas. It should be noted that the samples selected as 'reference' sites have PCB values ~2x higher than the PCB values taken as regional background levels from a larger study, although the reference samples reported here were collected near the regional reference sites. This points out a difficulty in using 'reference' samples or values – areas are heterogeneous, and comparisons are subject to the 'luck of the draw' when sampling. In any case, if PCBs are weighted this heavily, information on other COPCs becomes irrelevant, and all areas of sediment which were examined can be deemed of concern. While some areas have significantly higher HQ sums, and are thus potentially of greater concern (as was already clear from Fig. 3(a)), strict adherence to the presumption that PCBs should be managed to background levels suggests that all areas sampled in these transects require management or removal. Since this then entails hundreds of acres, the potential costs are enormous.

What SQGs are appropriate at a given site depends upon risk models used, the priorities of the stakeholders involved, and the questions being asked of the sediment. In the figures, we showed COPC distributions in the sediments relative to regional reference levels, ER-L and ER-M levels. Another approach which can be applied is not to compare sediment to these, but rather to generate site-specific benchmark values based upon site chemistry and bioassay results. Contaminant levels in sediments at the site can be compared with toxicity assays, bioaccumulation or flux measurements in the same sediments. If correlations are observed, 'acceptable' contaminant levels can be selected for a site.

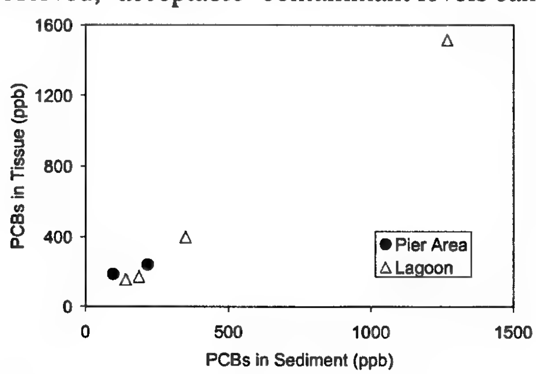

Fig. 4(a) PCB uptake in Macoma clam tissue vs. PCBs in sediments measured in lagoon and pier transect sediments

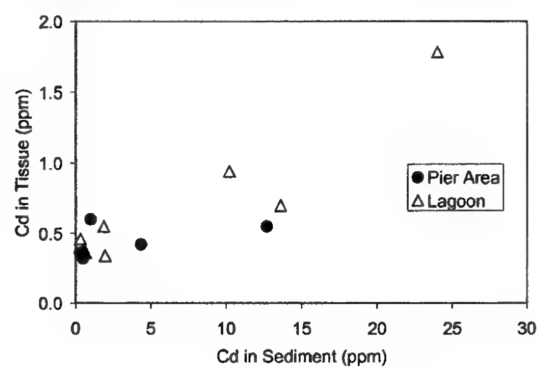

Fig. 4(b) Cd uptake in Macoma clam tissue vs. Cd in sediments measured in lagoon and pier transect sediments

As an example, Chadwick *et al.* (2000) observed at this site that Cd fluxed out of sediments, and that Cd remobilisation showed a strong correlation with both sediment Cd concentrations and bioaccumulation of Cd in Macoma clams, which also correlated well with one another (Fig. 4b), both of which were measured in co-located samples. They concluded that direct sampling of metal fluxes allowed for the evaluation of the exposure pathway, of the relationship to bioaccumulation, and of the impact of flux on overlying water concentrations. While PCB fluxes were not successfully measured at this site, examination of the results reveals that PCB concentrations in sediments correlated with uptake in Macoma clam tissue

(see Fig. 4(a)). While bioaccumulation does not in itself indicate toxicity, it can be an indication of contaminant bioavailability, and be indicative of potential toxicity. In the absence of consistent correlations between sediment chemistry and toxicity measures, the correlations between sediment chemistry and both flux and bioaccumulation described above may provide one basis for proposing 'acceptable' levels of COPCs in a sediment in a risk management process. If 'acceptable' tissue levels for a COPC are agreed upon, then these values can be used as SQGs to generate HQs, and samples and COPCs can again be ranked.

If a critical group of stakeholders does decide to try to base management decisions on very low levels of PCBs, it may become critical to separate regional 'background' levels or sources of PCBs from site-specific sources. While this can be difficult, organic contaminants such as PAHs, PCBs and pesticides exist in the environment as mixtures of many individual compounds with distinctive signatures. The relative proportion of these compounds is a function of many factors including source, weathering, degradation and mixing. Figures 5(a) and 5(b) show examples of both site-specific and regional signatures of PCBs at the site. The outfall area of the lagoon (Fig. 5(a)) has a distinctive signature, with a dominance of congener 209 not observed at high levels in the regional background sediments (Fig. 5(b)). Characterisation of these contaminant signatures in potential sources, sediment units, background sediments and bioaccumulating organisms may provide insight into local and regional sources, as well as potential recovery or risk processes. By collecting congener data initially, rather than just Aroclor data, it is possible to examine signatures where necessary. This information might be critical to identifying sources and management options.

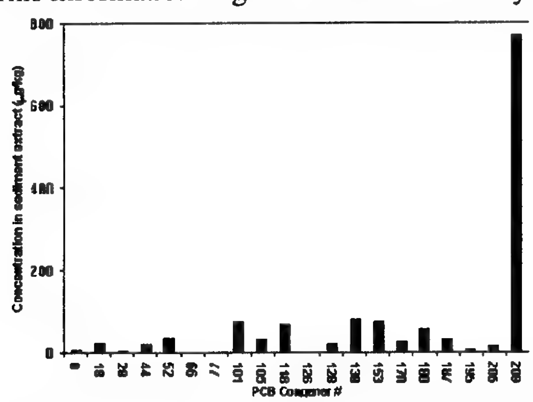

Fig. 5(a) PCB congener signature in a sediment unit from lagoon, northwest corner.

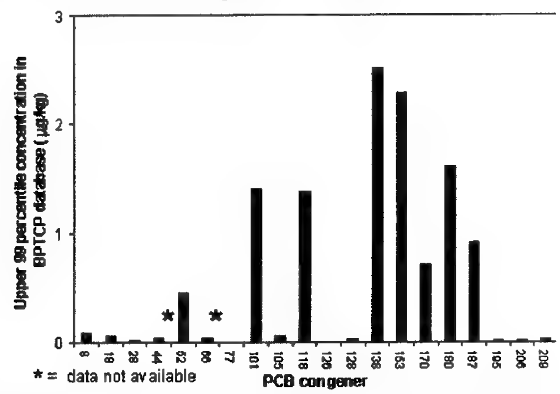

Fig. 5(b) PCB congener signature from reference sediments in the region.

CONCLUSIONS

The above discussion describes a subset of possible ways to represent data. With multiple potential risk drivers and management goals, the permutations are endless, and can be used to discuss the potential impacts of various approaches. Stacking bars allow for the visual interpretation of relative contributions of various COPCs. While not shown in this paper, other factors, such as toxicity assays, can be ranked in various ways and included in these plots. If data density is sufficient, once a set of reasonable parameters is agreed upon, results (hit sums, HQ sums, etc.) can be contoured on maps to delineate the geographic extent of impacted sediments. These maps can be compared to similar contour plots of other parameters such as individual COPC levels, sediment characteristics such as grain size, organic content, property lines or ecological zones, to help develop site conceptual models.

Information on volumes of sediment deemed to be of concern is necessary for its management. Thus, cores can be collected, and either analysed with depth, or homogenised

and analysed as samples representing sediment units, depending upon the management goal (e.g., Apitz *et al.* 1999). Ideally, if resources allow, data should be collected with depth to maximise three-dimensional information about sediment composition, and then integrated or averaged to predict 'whole volume' results. If sediments are to be dredged, it is important to know depth of contamination. However, mass balance calculations on sediment volumes can lend insight into the consequences of the removal or containment of given units of sediment.

This paper provides some examples of how sediment chemical data can be manipulated and plotted to aid in the negotiation of management strategies between multiple stakeholders. Sediments are very complex, and many aspects of a site must be considered in ecologically-sound, cost-effective sediment management. Generating data which can be used in many steps in the decision process, storing those data electronically to allow for multiple, and possibly unanticipated manipulations of the data to address various concerns, and graphically addressing the concerns of all stakeholders with a common and accessible dataset will aid in the negotiation and decision process.

ACKNOWLEDGEMENTS

Data analysed here were part of a baseline ecological risk assessment and technology validation carried out at the site by SSC San Diego and PRC Inc. (currently TetraTech EMI). PCB signature analyses were provided by Arthur D. Little, Inc. This work was funded by the Office of Naval Research, and NAVFAC Y0817. We than Ernest Arias for review comments.

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GIS – A Tool for Managing Contaminated Sites and Abandoned Stations in Antarctica

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ABSTRACT: The primary aim of this project is to develop an online prototype geographic information system (GIS) in consultation with the Australian Antarctic Division (AAD) to improve management during contaminated site remediation of an abandoned station – Wilkes Station. Geographic information systems can play an important role in the assessment and management of complex contaminated sites. Environmental managers and site remediation specialists increasingly rely on GIS technology to assist them during the decision-making process (Defina *et al.* 1998). This paper proposes to convey the importance of GIS as a tool for the successful and meaningful management of contaminated sites.

KEYWORDS: geographic information system, contaminated sites, Antarctica, environmental management

INTRODUCTION

The contaminated sites identified thus far in Antarctica are complex in nature and often extensive in area and volume. They are also geographically remote and technically and logistically difficult to manage. For these reasons no single management strategy is suitable for all sites. Presented with such complexity and the vagaries of Antarctic operations, and because it will take many years to remediate even the highest priority environmental risks, a precise data management system is essential.

The data collected have a strong spatial component so that the development of a geographic information system (GIS) can be considered as the locus of information processing, decision-making and remediation management. GIS is not only a tool for visualising site conditions and displaying results, it also has the additional advantage of being a spatial analysis tool that can be used to analyse data and to model processes, such as contaminant release pathways (Babicka *et al.* 2000).

Known sample sites can be spatially analysed to interpolate contaminant concentrations between sites and provide contour maps of contaminant distribution patterns to identify hotspots for further investigation. Data on contaminant levels can also be monitored spatially and temporally before, during and after cleanup or remediation.

GIS is a powerful tool for the evaluation of site data. A GIS-based data management system is an integral part of the quality assurance/quality control system associated with contaminated sites management. It provides an accurate record of contaminant levels at all stages of management, and allows critical assessment or validation of the chosen management strategies (Babicka *et al.* 2000).

In addition to providing an online data-management tool, the spatial analysis component of GIS can be used to delineate catchment boundaries, derive drainage patterns and define groundwater flow. This information can be used to predict contaminant dispersion and likely environmental impacts in the receiving environment. Information on drainage patterns can also be used during cleanup to indicate how best to manage water flow through

the site, for example, by diverting water courses away from areas where soils with high levels of contaminants are exposed (Snape *et al.* submitted).

CASE STUDY – WILKES STATION, EAST ANTARCTICA

Wilkes is an abandoned Antarctic Research Station situated on Clark Peninsula (66°15'30S, 110°32'E) 3 km north of Casey Station. Constructed by the USA for the International Geophysical Year (IGY) 1957-1958, administrative and operational control was handed over to Australia at the end of the IGY in February 1959. Wilkes was occupied by the Australians until 1969 when snow accumulation prompted the construction of Old Casey Station.

Snape *et al.* (1998) documented 39 contaminated sites at Wilkes and compiled a preliminary contaminated sites' register to assess a means by which to further define the impact at Wilkes. It was recommended that a web-linked GIS be developed to address the need for improved documentation of site investigation, evaluation and management. Figure 1 illustrates how this might be achieved

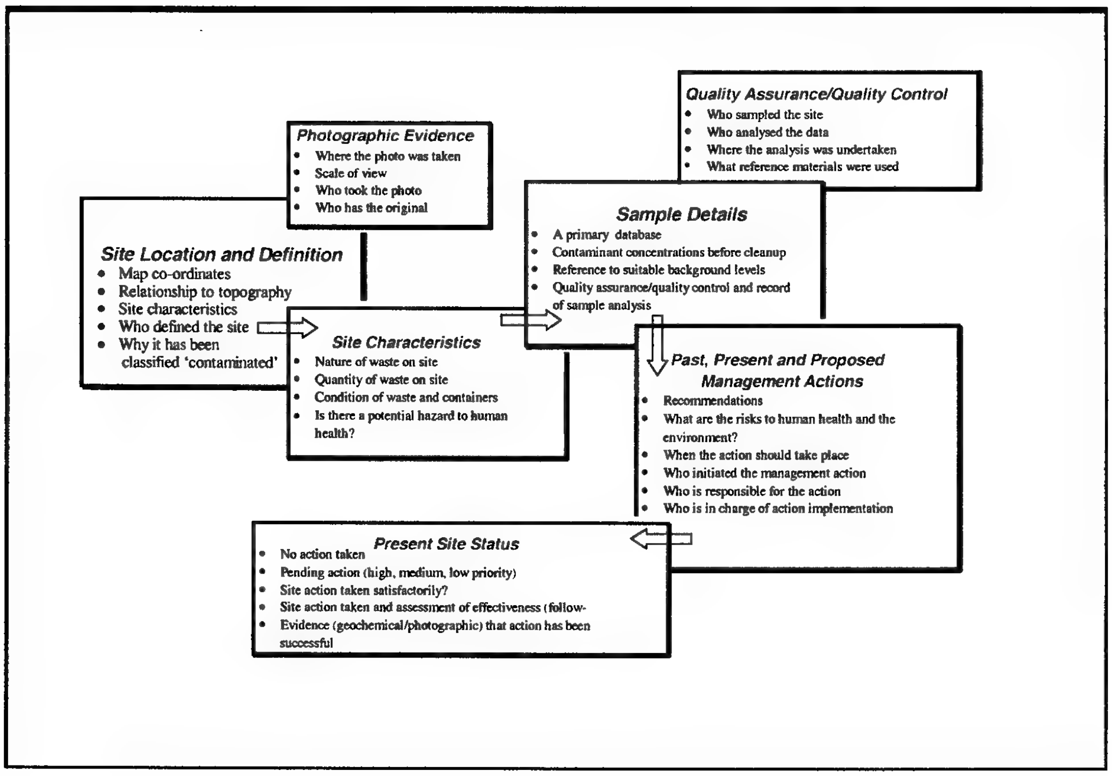

Fig. 1. Schematic representation of on-line GIS (after Snape *et al.* 1998)

RESULTS

A detailed site survey was commenced in the 1998-99 summer field season to gather data. During this time all visible major items of debris and sources of contamination were surveyed, positions recorded using a GPS unit (Trimble GPS and TDC2 data logger), with 8 fixes at a 15-s frequency. Positions were differentially processed with reference GPS data

collected at the Casey GPS base station (Ashtech) using Pathfinder Office software and exported into ArcView GIS software developed by ESRI (Environmental Systems Research Institute, Inc., 380 New York Street Redlands CA 92373, USA). Sources of contamination include leaking or rusty fuel drums, discarded lead acid batteries and chemical drums (including caustic soda).

Data Integration into GIS

Differentiated point, line and polygon features were entered into the GIS along with attribute data of the features. For example the contents, volume and condition of fuel drums at the Wilkes Fuel Farm site. These data were further supplemented with field observations, photographs and historical notes.

At a fundamental level the GIS can be queried to display the co-ordinate positions of all high priority removal items, which may be considered an advantage from an operational view point. These items may include leaking, rusty fuel drums, solvent or chemical drums (Fig. 2). The same thematic layer may be interrogated to display the contents of fuel drums (e.g. diesel, SAB, aviation fuel), associated volumes and the condition of the drums themselves. Similarly heritage items can be located for retrieval and restoration purposes.

The web-based GIS will include baseline information such as topography, geomorphology and biota of the region. Superimposed on these thematic layers, major items of debris can be simultaneously categorised by criteria such as waste type, associated hazards, cleanup priority, heritage value, and waste management stream.

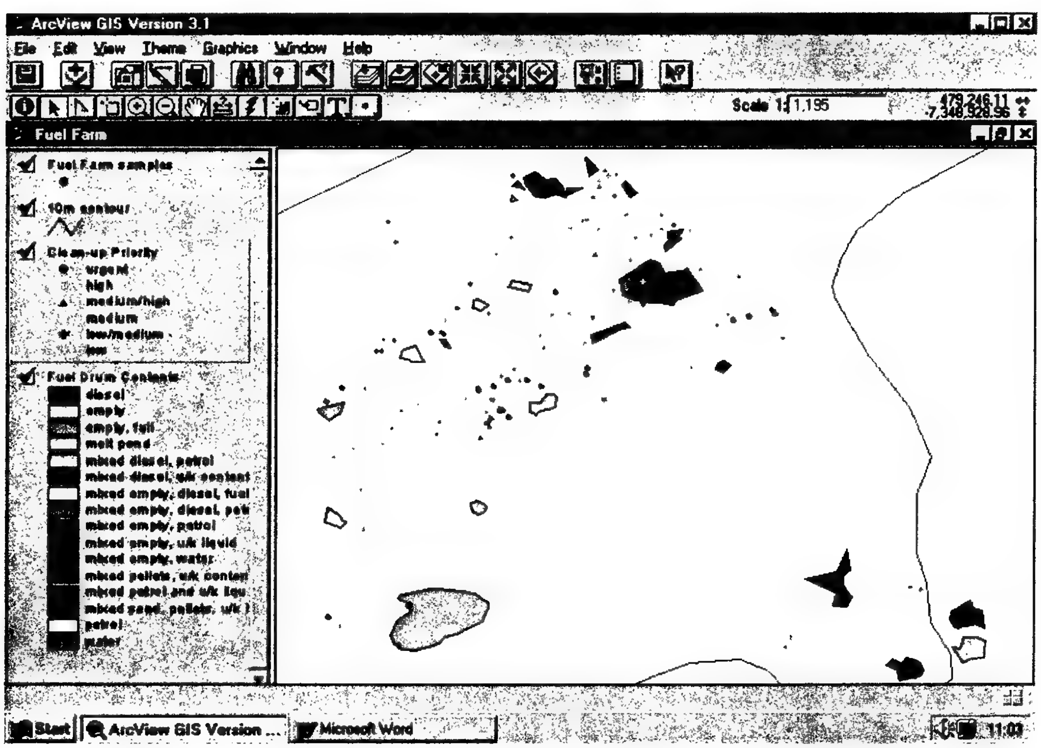

Fig. 2. Example of ArcView screen showing fuel farm at Wilkes Station

Further information about the on line Wilkes Station contaminated sites GIS can be obtained from the Australian Antarctic Division's website:
http://www-aadc.antdiv.gov.au/human_impacts/wilkes/contaminated_sites.html

DISCUSSION

Any large-scale cleanup operation will undoubtedly be of interest to many stakeholders It is hoped that the GIS will facilitate the role of managers in the decision making process to be better able to prioritise sites for remediation, assess the suitability of removal and remediation techniques, and develop site-specific management strategies.

The public wants to see the unique wilderness qualities of the Antarctic preserved and protected. The cleanup of Wilkes will demonstrate the commitment Australia has to:

a) protecting the Antarctic environment;
b) meeting international obligations;
c) best practice in environmental management.

A web-based GIS enables all stakeholders, both within the AAD and external parties to access information and achieve these goals.

In view of government priorities for Antarctica and obligations under the Madrid Protocol, the geographic information system developed will improve documentation procedures and provide accessible, up-to-date documentation of spatially referenced data to site managers, site workers and environmental decision makers. GIS allow the AAD to use and update its contaminated sites data more efficiently and future development of temporal layers from archived aerial photos and future cleanup operations will allow the GIS to be interrogated on a temporal as well as a spatial scale.

CONCLUSIONS

Geographic information systems provide an accurate and valuable tool to assist in the management of complex contaminated sites. The ability to combine large amounts of descriptive and spatial data into a system that is quickly and easily queried by on-site managers allows the flexibility to simultaneously assess and manage various waste streams during site cleanup and remediation. The GIS facilitates the role of managers in decision-making and enables them to easily prioritise sites for remediation, assess the suitability of removal and remediation techniques, and develop site-specific management strategies.

The capability of GIS to perform spatial operations that calculate the extent of contamination and approximate contaminant volume can ultimately enhance our understanding of relative contaminant distributions and dynamics of the system.

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The Effect of Sampling Variables on the Concentration of Analytes in Landfill Leachate

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ABSTRACT: A study was undertaken to determine a reliable sampling methodology that produces representative municipal waste landfill leachate samples for laboratory analysis. The effects of two key sampling variables, type of sampling location (leachate collection sump *vs* bore into landfill) and sampling equipment (bailer *vs* bladder pump) on leachate quality were investigated by statistical analysis of laboratory results for numerous chemical parameters. Spatial heterogeneity of waste and leachate composition appears to be the controlling factor on leachate composition regardless of the type of sampling location (leachate sump or from a nearby bore). Statistically significant differences in concentrations of some parameters were identified between samples collected with a bladder pump compared to those collected with a bailer (collected from the same bore within a landfill cell). Increased volatilisation and turbidity of bailed samples compared to those collected with a bladder pump appear to be responsible for these differences. The results of this study show that although a bladder pump used within a bore drilled into the landfill will provide more reliable geochemistry, a point within the leachate collection system (e.g. sump) provides a more representative sample of leachate from a broader area of the landfill.

KEYWORDS: landfill, leachate, sampling

INTRODUCTION

There is a growing number of studies of leachate composition from varying types of landfill (e.g. Chian and DeWalle 1977, Christensen *et al.* 1993, Ehrig 1983, Forst *et al.* 1989, Gintuatas *et al.* 1992, Hancock *et al.* 1995, Harmsen 1983, Miriki and Parks 1994, Murray and Beck 1990, Öman and Hynning 1991, Ragel *et al.* 1995, Schultz and Kjeldsen 1986). These studies mostly focus on the analytical results in order to characterise leachate quality and seldom mention the sampling methodology. The nature of municipal waste landfill leachate suggests that processes such as volatilisation, degassing, oxidation and sorption may result in unrepresentative samples being collected and therefore unrepresentative analytical results.

Various authors have identified the significance of sampling variables in groundwater studies and some leachate studies. Öman and Hynning (1991) state that an important factor in influencing analytical results (of organic compounds in landfill leachate), besides analytical method, is the sampling point. According to Barcelona (1995), field sampling (of groundwater) can often be the most significant source of error in determining analytical results that are representative of field conditions. There is, however, no broadly accepted methodology for the collection of leachate samples that produces comparable analytical results. An understanding of the effect of sampling variables on analytical results is paramount in the development of a methodology for sampling leachate that will result in more reliable and readily comparable data of the composition of landfill leachates.

It is expected that the location of sample collection as well as the device used will be the most significant influences on resultant leachate composition. As part of a broader study of the chemical composition of leachates from two 'modern' municipal waste landfills, the effects of two key sampling variables, type of sampling location (leachate collection sump *vs* bore into landfill) and sampling equipment (bailer *vs* bladder pump) on leachate quality were investigated by statistical analysis of laboratory results for numerous chemical parameters. The objectives of the investigation were to document the effects of sampling variables and make recommendations with respect to a landfill leachate sampling methodology.

METHOD

Two landfills in metropolitan Melbourne, Victoria, Australia (Clayton South and Brooklyn) were selected for this investigation. These are 'modern' municipal waste landfills in that they receive putrescible and solid inert wastes (but not soluble chemical, hazardous, liquid or prescribed industrial wastes) and are designed and constructed to minimise environmental impact.

Type of Sample Collection Location

The investigation aimed to determine if there is any significant difference in the composition of leachate collected from leachate collection sumps (local practice) compared to that collected from bores drilled directly into a landfill cell. While both types of sampling locations are situated within the landfill (to minimise alterations to the leachate caused by sorption, oxidation from contact with air or dilution by groundwater), leachate collection sumps have a much larger atmospheric interface. This allows a greater opportunity for interaction between leachate and the atmosphere, possibly causing a loss of volatiles, degassing and the introduction of oxygen. Sumps also collect leachate from large areas of landfill cells. By contrast, bores have much smaller atmospheric contact and samples from bores are drawn from their immediate vicinity.

Equipment used to Collect Leachate Samples

The investigation also aimed to determine if there is any significant difference between leachate samples collected using a bailer and those collected using a bladder pump. Currently, all landfill leachate sampled from within landfills in Victoria is collected using a bailer. International literature casts doubt over the ability of bailers to recover representative samples as they can impact on volatile analytes and analytes that are readily oxidised and thus subject to precipitation reactions (Parker, 1994). Further, sampling with bailers has been found to increase turbidity, causing elevated concentrations of metals and hydrophobic organics (Parker, 1994). The same research has found that, generally, bladder pumps gave the best overall recovery of the sensitive constituents of all devices tested (Parker, 1994).

Investigation Design

Replicate samples (four) were collected for each sampling sub-set (e.g. bladder pump) as shown in Table 1. The investigation of the effects of the type of sample location on leachate analyte concentrations was undertaken at Brooklyn landfill (see Table 1). The leachate collection sump and leachate monitoring bore used in this experiment are located within the

same landfill cell, approximately 50 m apart. Samples were collected from both types of sampling location using bailers.

The investigation of the effects of sampling equipment on leachate analyte concentrations was undertaken at Clayton South landfill. Leachate samples were collected consecutively from the same bore drilled into a completed landfill cell specifically for leachate quality sampling.

Table 1. Investigation design, showing the number of replicate samples from each type of sample location using a bailer and bladder pump

	Sump		Bore	
Landfill	*Bailer*	*Bladder Pump*	*Bailer*	*Bladder Pump*
Clayton South	NA	NA	4 [1]	4 [1]
Brooklyn	4 [2]	NA	4 [2]	NA

Note: [1] For comparison of Sampling Equipment. [2] For comparison of Type of Sampling Location
NA – Not Applicable

Samples for both experiments were collected between 20/2/98 and 12/3/98. Important features of the sampling procedure include:

(a) low flow (<500 mL^{-1} min) purging/pumping in conjunction with leachate quality stabilisation criteria for field measurements (e.g. electrical conductivity, pH, oxidation/reduction potential) when sampling with the bladder pump;
(b) samples collected for heavy metals analysis with the bladder pump were filtered (0.45 μm) 'in line' then preserved upon arrival at the laboratory, while samples collected for heavy metals analysis with bailers were filtered and preserved upon arrival at the laboratory.

Samples were analysed for a total of 92 individual analytes, including major ions, heavy metals, bulk organics (e.g. total organic carbon), phenolic compounds, volatile fatty acids, alcohols, chlorinated hydrocarbons, monocylcic aromatic hydrocarbons, semi-volatile organic compounds (e.g. o-cresol) and pesticides (organochlorine and organophosphate). Quality control samples (blind duplicates and equipment rinsate blanks) were collected and analysed to assist in assessing the reliability of the data.

Statistical Analysis of Results

Statistical analysis of laboratory results was used to determine the significance of differences in parameter concentrations between municipal waste leachate samples collected:

(i) from *two types of leachate sampling location within the one landfill cell* (bore and sump in cell of Brooklyn Landfill); and also
(ii) *by two types of sampling equipment used at a single sampling location*(bailer and bladder pump).

T-tests (two-tailed) were conducted for each chemical parameter and sampling variable. This statistical test returns the probability (p) that the samples from different populations have the same mean. A significance level of 0.05 was selected. That is, where the probability that samples from different populations have the same mean is less than 0.05 ($p<0.05$), there is a significant difference between the two sample populations. T-test calculations assuming both unequal (heteroscedastic) and equal (homoscedastic) variance between sample populations were conducted. Equal variance was assumed in the few cases where the standard deviation

of one sample population (for one sampling variable, for example 'bailer') was less than twice that of the other.

RESULTS

Most analytical parameters did not show significant differences according to either sample location or sampling equipment. The probability (p) of differences in chemical parameter concentrations caused by the sampling variables is between 0.05 and 0.95 (i.e. not significant) for most parameters, suggesting a high degree of natural variability in the samples as well as the low number of sample replicates. Of all the individual chemical parameters, statistically significant and reliable differences were found in only 14 analytes according to type of sampling location and only 10 analytes according to sampling equipment. Table 2 is a summary of the analytical parameters affected by the sampling variables.

Table 2. Summary of statistically significant and reliable differences in chemical parameters according to sampling variables

Sampling Variable – Type of Location			*Sampling Variable - Equipment*		
Analytical Parameter	Sump	Bore	Analytical Parameter	Bailer	Pump
pH		✓	pH	✓	
TDS	✓		K^+	✓	
Ca^{2+}	✓		Fe	✓	
Mg^{2+}	✓		Cr	✓	
K^+	✓		Zn	✓	
Na^+		✓	Ethanoic acid	✓	
Methanol		✓	Ethyl benzene		✓
Ethyl benzene		✓	*m/p*-Xylene		✓
m/p-Xylene		✓	*o*-Xylene		✓
o-Xylene		✓	1,8 Cineole	✓	
Alpha Thujone		✓			
1,8 cineole		✓			
n-butyl-benzenesulfonamide		✓			
1,4-DCB		✓			

✓ Sample location or equipment with significantly higher analyte concentrations (or pH value)

DISCUSSION

The Effect of Type of Sampling Location on Analyte Concentrations in Landfill Leachate

It was expected that leachate collected from a sump compared to that from a bore would be less representative of 'in landfill' conditions, due to the larger atmospheric interface at the sump and the resulting increased opportunity for volatilisation, degassing and oxidation. While some differences in parameter concentrations, such as the volatile ethylbenzene and the xylene isomers are consistent with this hypothesis, the differences in leachate parameter concentrations between the sump and bore are not considered to be due to the type of sample location.

Instead spatial heterogeneity of waste and waste stabilisation (due to the landfilling practice of creating small isolated cells of waste) appears to be the controlling factor on leachate composition, regardless of whether leachate is collected from a sump or bore. This is supported by a high degree of spatial heterogeneity in leachate composition (inorganic and organic parameters) observed at Brooklyn Landfill between other bores completed into this landfill that were not part of this experiment. The spatial heterogeneity in leachate composition is also consistent with the findings of Kjeldsen *et al.* (1993). Therefore, although sampling related literature suggests that a leachate sump will not provide representative samples because of chemical and physical processes at the atmospheric interface, this was not substantiated by this study. Instead, spatial heterogeneity of waste and leachate was the controlling factor.

In order to adequately investigate the effects of sampling location type on leachate analyte concentrations the effects of spatial heterogeneity must be overcome. To achieve this, both sampling locations (sump and bore) would have to be located very close to each other (<5 m) in the same cell of daily waste. Ideally, such an experiment would involve a greater number of samples to increase the statistical strength of the test, and sampling parameters would concentrate on those sensitive to degassing, volatilisation, oxidation and sorption.

The Effect of Sampling Equipment on Analyte Concentrations in Landfill Leachate

The volatile monocyclic aromatic hydrocarbons (MAHs) ethylbenzene, *m/p*-xylenes and *o*-xylene were present at significantly ($p<0.05$) higher concentrations in samples collected using the bladder pump (Table 2). Figure 1 shows that the mean concentrations of these MAHs in bailed samples were 33% to 38% lower than in samples collected with the bladder pump.

These results are similar to the 29% to 36% loss of volatile organic compounds in bailed samples measured by Blegen *et al.* (1988), and are within the range of <5% to 88% (losses of volatiles in bailed groundwater samples) noted by Parker (1994). As the samples of this investigation were collected consecutively from the same location, the data from Clayton South Landfill indicate that volatilisation of these compounds occurs during bailing.

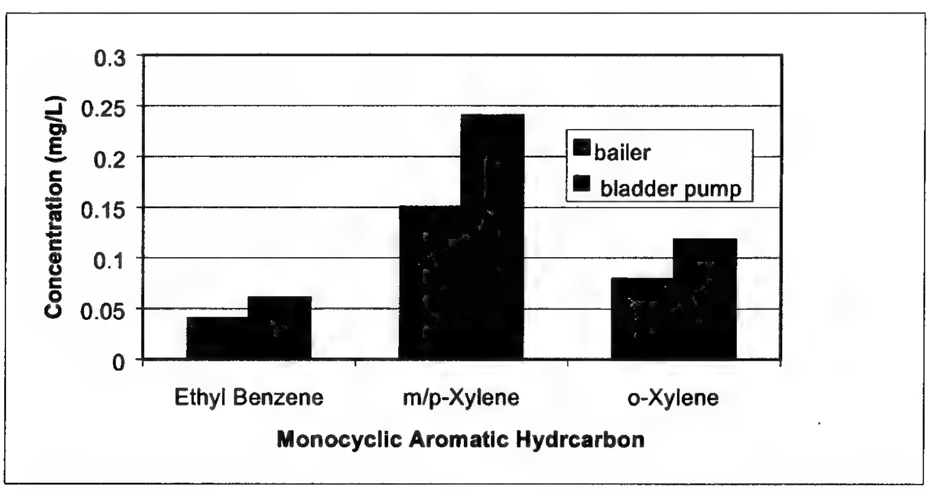

Fig. 1. Mean concentrations of some monocyclic aromatic hydrocarbons in leachate sampled with a bailer and bladder pump at Clayton South Landfill

The major ion K^+ and the heavy metals Fe, Cr and Zn display significantly ($p<0.05$) higher concentrations in bailed samples. Mean bailed sample concentrations for these parameters ranged from 134% (K^+) to 494% (Zn) those of (bladder) pumped samples. Figure 2 shows this relationship for the heavy metals Fe and Zn (the concentrations of Cr are too low to be seen on this graph). Although not significant ($p = 0.06$ to 0.07), the metals Cu, Ni and Hg displayed the same trend as Fe, Cr and Zn.

These results are not consistent with other studies such as Mabey and Barnes (1995) and Pohlmann *et al.* (1995) who found no significant difference in metal concentrations between filtered bailed and filtered pumped groundwater samples (generally <10%). It is possible that the action of bailing leachate brought solids into suspension (with attached heavy metals and K^+) that are capable of passing the 0.45-μm filter. Again, this is inconsistent with Pohlmann *et al.* (1995) who found that >96% of solids brought into suspension by bailing (groundwater bores in low permeability formations) were >0.45 μm and therefore too large to pass the filter. This inconsistency may be caused by a greater abundance of smaller (<0.45 μm) colloids (possibly organic) in the landfill leachate than in groundwater from low permeability formations. The increase in turbidity due to bailing is thought to also be responsible for the statistically significant higher concentrations of ethanoic acid and 1,8 cineole in bailed samples.

An increase in pH was the only statistically significant evidence that bailed samples degassed more than those sampled with the bladder pump, while no effects of oxidation of bailed samples were observed. The results do not indicate that processes such as oxidation and degassing are not occurring, only that they are not evident enough to be detected by the statistical test. The high variability of the data decreases the likelihood of significant relationships being detected. A more thorough investigation of the effects of sampling equipment on leachate composition could be undertaken using a greater number of replicates for each type of sampling equipment.

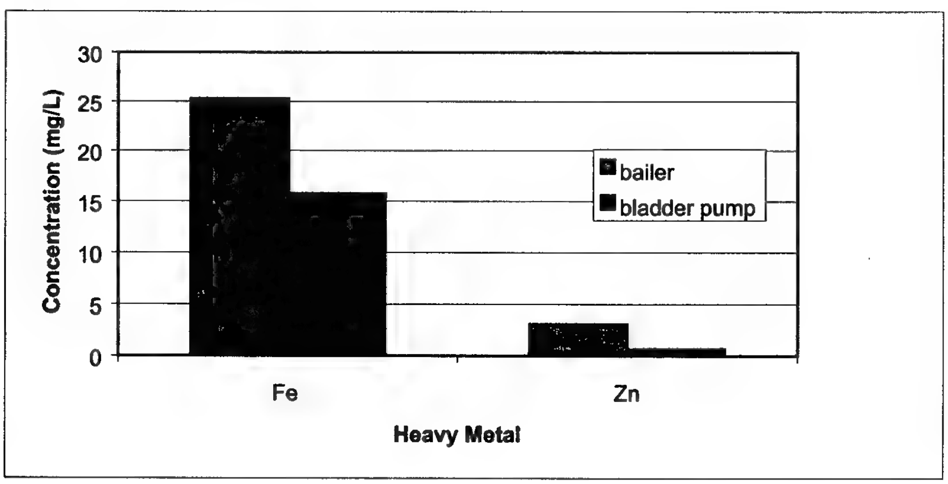

Fig. 2. Mean concentrations of Fe and Zn in leachate sampled with a bailer and bladder pump at Clayton South Landfill

CONCLUSIONS

Spatial heterogeneity of waste and leachate composition appears to be the controlling factor on leachate composition regardless of the type of sampling location (leachate sump or from a nearby bore). Bores constructed directly into landfill cells are most likely to produce the least altered leachate samples for analysis, however they produce samples from a very localised area that may not be representative of the landfill. Leachate collection sumps are connected to a system of drains that collect leachate from a wider area of the landfill and, provided they are sealed between sampling events (to minimise degassing and volatilisation), are expected to produce a sample that is more representative of the landfill. On this basis, leachate collection sumps (that are effectively sealed between sampling events) are the recommended leachate sampling locations.

Statistically significant differences in concentrations of some parameters were identified between samples collected using a bladder pump compared to those collected using a bailer (collected from the same bore within a landfill cell). Increased volatilisation and turbidity of bailed samples compared to those collected with a bladder pump appear to be responsible for these differences. Despite this, the significant difficulties in sampling with a bladder pump from the recommended sampling location (i.e. leachate collection sump that is effectively sealed between sampling events), such as clogging and insufficient head to drive leachate into the pump as the type of sampling location, result in bailers being the most feasible sampling equipment. It is therefore recommended that light weight, bottom loading bailers (with emptying device) be used to sample landfill leachate, provided extreme care is taken to minimise sample disturbance.

Further work in this area should focus on a few analytes most likely to be affected by the sampling variables (e.g. volatile compounds) and have a higher number of sample replicates than used by this study.

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First In, Last Out: Should Aquifer Ecosystems be at the Vanguard of Remediation Assessment?

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ABSTRACT: Diverse assemblages of invertebrates are obligate inhabitants of groundwater which, with microbial and protozoan communities, occasionally vertebrates, comprise groundwater ecosystems. They are found to one kilometre depth in karstic, alluvial and fractured rock aquifers and may depend on allocthonous or chemoautotrophic energy sources, and may be found under oxic and anoxic conditions. Groundwater ecosystems may be comparable in diversity and dynamics to some surface ecosystems. The maintenance or recovery of groundwater ecosystems should be the goal of groundwater management and site remediation, as in surface ecosystems. Stygofauna may serve as sentinels for groundwater contamination and as indexes of restoration. They may influence restoration work directly through their physical activity or indirectly through their ecological interactions with microbial communities. By focussing on the ecosystem rather than the contaminant there are possible circumstances under which restoration may be contraindicated. It may be useful to include the status of groundwater as a contaminant.

KEYWORDS: groundwater ecosystems, invertebrates, stygofauna, sentinels, restoration.

INTRODUCTION

The potential role of invertebrates, largely crustaceans, is ignored in groundwater remediation studies. These, together with microbes and protozoa, comprise the aquifer ecosystems that are the first to be impacted by groundwater contamination, and may be the last to be relieved of its consequences. Hence, aquifer ecosystems, or their members, may serve both as an indicator of the onset of contamination and of their eventual remediation. Just as in surface ecosystems, should the restoration of aquifer ecosystems be the ultimate measure of groundwater remediation?

I present a brief background to groundwater ecosystems and discuss the possible utility of considering the restoration of groundwater ecosystems as a goal in remediation work, rather than the usual restricted scope of removing the contaminant(s), albeit sometimes utilising microbial means. While making reference to the key world literature, where possible I draw on indicative Australian studies and, for brevity, often cite only the volume in edited works.

SUBTERRANEAN ECOSYSTEMS

Life forms may occur several kilometres below the Earth's surface and this subterranean world is the largest terrestrial biome (Gold 1992). A specialised invertebrate fauna, occasionally vertebrates, occurs in these subterranean ecosystems, the health of which is paramount as the greater part of the world's freshwater occurs as groundwater. My references to groundwater ecosystems incorporates this wider view of subterranean ecosystem, rather than the microbial, occasionally protozoan, assemblages usually referred to in the context of remediation work. However, in some aquifer ecosystems only microbial elements will occur.

Animals are mostly restricted to the upper parts of subterranean ecosystems, that region commonly the target of remediation work. Nonetheless, a diverse stygofauna (Longley 1992) may be found up to at least one kilometre depth (Essafi *et al.* 1998); stygofauna is known in Australia from between 1 and 150 m depth (Humphreys 2000).

Subterranean waters are conveniently separated into groundwater and hyporheic waters that occur below river channels (Jones and Mulholland 2000) forming a broad ecotone between surface water and groundwater. Stygobites are the obligate inhabitants of groundwater, collectively comprising the stygofauna (Gibert *et al.* in Gibert *et al.* 1994). Stygobites have a convergent morphology - distinct from the vermiform tendencies of interstitial fauna - exhibiting a reduction or loss of eyes, pigments and hardened body parts (they are commonly translucent), and they have enhanced non-optic sense organs (Culver *et al.* 1995). Stygofauna tend to be slow-growing, long-lived and have few young, attributes that make them difficult to study but efficient bioaccumulators (Plenet *et. al.* 1992) and slow to recover from reductions in their populations. Groundwater ecosystems are not semi-deserts, occupied by rare, effete lineages, but are dynamic systems comparable in complexity to surface ecosystems (Rouch 1977, Gibert *et al.* 1994).

Groundwater ecosystems commonly comprise locally endemic species (species restricted to a small geographic area) and may include species belonging to ancient relictual lineages. In northwestern Australia, stygal assemblages occur that largely comprise lineages known elsewhere only from groundwaters on either side of the North Atlantic — they are surviving Mesozoic communities (Humphreys 2000). Other stygofaunas comprise lineages distributed amongst fragments of the supercontinents (Poore and Humphreys 1998, Wilson and Keable 1999). Despite widespread relict geographical and phyletic lineages, there is also active colonisation of stygal habitats and some lineages may repeatedly enter or emerge from the stygal systems through evolutionary time (Culver *et al.* 1995).

Types and Locations of Groundwater Habitats

Groundwater ecosystems are of wide extent, occurring in karst, basalt, alluvial and in fractured rock matrices (Malard *et al.* 1996). Karst systems are typically of restricted extent, especially in Australia, and the contained stygal inhabitants may be confined to a particular cave or karst region (Wilkens *et al.* 2000). In contrast, alluvial aquifers may form a system of interconnected pathways that through time form a global pathway of dispersal (Stanford and Ward 1993), comparable to that proposed to follow the mid-oceanic ridges (Boxshall 1989).

Australia has the usual array of karstic and alluvial aquifers containing stygofauna (Humphreys 1999a, Hamilton-Smith and Eberhard in Wilkens *et al.* 2000). But, in addition, there are anchialine systems (near coastal groundwaters influenced by marine tides but without surface connection with the sea (Humphreys 1999b)) as well as novel faunas in both fresh and saline groundwater calcrete aquifers (Humphreys 1999a, in press).

Globally, aquifer ecosystems were best studied in karst regions of carbonate rocks which characteristically exhibit open conduit flow that causes the particular remediation problems associated with non-Darcian systems. Recent research has focussed on alluvial aquifer ecosystems, owing to their potential impacts on surface water and their perceived role in protecting groundwater from contaminants (Gibert *et al.* 1994, Jones and Mulholland 2000).

Anchialine systems exhibit sharp clines in temperature and salinity below which occur layers of hydrogen sulphide, sub- to anoxic conditions, chemoautotrophic energy production and a specialised fauna (Humphreys 1999b, Pohlman *et al.* in Wilkens *et al.* 2000) that is vulnerable if the stratification is disrupted. Remediation work would need to maintain the vertical stratification of the ecosystem and this requirement may generalise to any system

exhibiting marked stratification, such as found in calcrete aquifers in the Australian arid zone (Watts and Humphreys in press, Humphreys in press).

Groundwater Ecology in Australia

In the late nineteenth century Charles Chilton, working mostly in New Zealand and Australia, was a global pioneer of groundwater biology (Hurley 1990). However, the groundwater fauna (stygofauna) of Australia, together with that of Africa, is now especially poorly known (Marmonier *et al.* 1997). Most work has been conducted on cave faunas (Hamilton-Smith and Eberhard in Wilkens *et al.* 2000, Humphreys 2000) and work other than in caves is recent (Humphreys 1999a, in press). A measure of the poverty of information can be drawn from Australia having changed within the last decade from being considered depauperate in stygofauna to being stygofauna rich. For example, Australia has the world's two most species rich stygal amphipod communities, Barrow Island (an anticline of Miocene limestone), and at Ethel Gorge, a groundwater calcrete deposit of Tertiary age on the Fortescue River. Furthermore, a small part of the Western Shield contains more species of stygal diving beetles (Dytiscidae) than the remainder of the world (e.g. Watts and Humphreys in press).

Apart from faunistic studies, there is meagre knowledge of aquifer ecosystems in Australia. Some research has been conducted on an anchialine system (Humphreys 1999b) and on hyporheic systems (Boulton in press), peripheral to groundwater ecosystems. However, even in the absence of detailed knowledge of Australian groundwater ecosystems, research elsewhere (e.g. Gibert *et al.* 1994), and general principles dictate that they provide 'ecosystem services' which is the reason for maintaining biodiversity rather than simply protecting endangered species. Interference with groundwater ecosystem 'services' in the absence of knowledge of the associated processes and dynamics may involve the risk of destabilising such systems.

Energy Sources

Until recently, subsurface microbial communities were thought to be supported by organic matter transported from the surface along flow paths or from organic matter deposited in sediments at their formation (Krumholz 2000). Over the last ten years, microbial communities have been found in a wide variety of situations, often deep into the earth's surface, and which are energetically dependent on non-traditional sources of energy (Table 1). Similarly, stygofauna has also been considered dependent on the downward percolation of energy fixed by the photosynthetic pathways of green plants which is processed by decomposers or trapped by the biofilm to form the foundation of the subterranean ecosystem. Recent work has shown that a variety of stygal ecosystems may also be dependent on energy derived *in situ* along chemoautotrophic pathways, being fixed, for example, by methanogens and sulphur bacteria. In the artesian Edwards Aquifer, Texas (Longley 1992), and in Movile Cave in Romania (Sarbu in Wilkens *et al.* 2000), sulphides, respectively of petroleum and magmatic origin, support chemoautotrophic ecosystems (Poulson and Lavoie in Wilkens *et al.* 2000). These ecosystems are analogous with those associated with both hydrothermal and cold deep sea vents (Gebruk *et al.* 1997). Chemoautotrophy has also been demonstrated in Frasassi Cave (Sarbu *et al.* in Wilkens *et al.* 2000), and strongly implicated in anchialine systems (Humphreys 1999b, Pohlman *et al.* in Wilkens *et al.* 2000).

Table 1. The location and energy sources of some subsurface microbial communities (Krumholz 2000)

Location	Energy source
1, Heterotrophic anaerobes	Permeable sandstone adjacent to organic-rich deposits (lignite rich Eocene sediments; organic rich Cretaceous shales and Cretaceous clays containing organic materials and fermentative bacteria.).
2, Igneous rock no organic source apparent.	Basalt and granite-rich subsurface (10^4-10^6 cells mL^{-1}; lithotrophic bacteria growing on chemically generated H_2.
3, Deep oceanic sediments	Anaerobic metabolism and sulphate reduction.

Groundwater ecosystems are generally energy poor and the addition of energy to the system can reduce the competitive advantage that stygofauna has under these oligotrophic conditions and permit the invasion of surface species (Malard *et al.* 1996). Contaminants may boost energy levels in groundwater and enhance microbiological (Haack and Bekins 2000) and probably macroinvertebrate productivity but excessive levels of organics, for example of sewage, may reduce populations (Sinton 1984). Although many contaminated sites are anaerobic as a result of bacterial utilisation of oxygen (Haack and Bekins 2000), this need not preclude the presence of macroinvertebrates as many stygal species are adapted to extremely low, even anoxic conditions (Hervant *et al.* 1998, Humphreys 1999b).

Function Role of Invertebrates

Recent studies suggest that the variability in subsurface geochemical and hydraulic conditions influence the subsurface microbial community structure (Haack and Bekins 2000) in a manner comparable to that found in stygal communities (see Gibert *et al.* 1994, discussion in Humphreys 1999b, Watts and Humphreys in press).

By analogy with surface ecosystems, invertebrates have numerous potential functionAL roles in groundwater systems, but as yet experimental evidence is largely lacking. These include the maintenance of voids — suggested also for protozoa (Haack and Bekins 2000) — the alteration of redox gradients, enhancing the release of organic carbon and the cycling of nutrients (which often limit bioremediation processes: Haack and Bekins 2000), promotion of biofilm activity (*inter alia* through grazing, nutrient cycling and improved hydraulic flow paths), the provision of favourable sites for microbial activity (see also Gebruk *et al.* 1997 below), the acceleration of cycling, movement and mass transfer of energy and materials through the sediments, alteration of population size and community structure through predation ('top-down' effects) and as prey ('bottom-up' effects). These issues are discussed and referenced more fully by Boulton (2000: Table II). While it is recognised that consortia of microorganisms can work, by mechanisms yet to be identified, to breakdown contaminant plumes (Haack and Bekins 2000), it has yet to be recognised that stygofauna may be expected similarly to interact with biofilms, and other expressions of microbial diversity, so as to promote or to restrict their activity and the community diversity in groundwaters.

Microbial Communities

Diverse microbial communities occur in groundwaters (Haack and Bekins 2000, Humphreys 1999b), and the complexity of these ecosystems is greatly enhanced by the presence of protozoans, which can reach densities of up to 10^4 g^{-1} in contaminant plumes. Predation by protozoans may control bacteria abundance (density of protozoa: bacteria is 1:

10^3) and structure microbial communities (Haack and Bekins 2000). Even in deep granite aquifers, sulphur bacteria may occur at densities of 10^4-10^6 cells mL^{-1} groundwater (Krumholz 2000) but it is not known whether their replication rate is sufficient to support stygofauna.

Microbial communities in groundwater are influenced by the strong vertical and horizontal geochemical gradients in the groundwater (Haack and Bekins 2000), analogous to the effect found in stygofaunal communities (Rouch and Danielopol 1997, Humphreys 1999b, Watts and Humphreys in press). These marked gradients require that the sampling intervals be determined at a scale appropriate to the gradients and sometimes this necessitates very fine scale spacing of sampling units (Humphreys 1999a). The presence of sharp gradients offers the potential for invertebrates (as well as microorganisms: *ibid.*) to sample across the interface into contaminant plumes otherwise inimical to life, even of utilizing microbial intermediaries, as occurs with some species utilising the hot vent ecosystems of the deep ocean; interfaces so marked that many shrimps may be scarred from the scolding water (Gebruk *et al.* 1997).

Stygal and hyporheic communities may also change on a fine scale due, for example, to sometimes subtle changes in hydraulic conductivity, water flow characteristics or oxygenation (Rouch and Danielopol 1997). Such work on invertebrates reinforces the work on subsurface microorganisms that substantiates the need to understand the structure of both communities and populations in contaminant plumes in order to interpret degradation processes (Haack and Bekins 2000). As subsurface bacteria and stygofauna coexist they are subject to many of the same conditions and constraints, but, because the studies are rarely juxtaposed either physically or intellectually, there is little interplay between the relevant research workers.

Ecosystem Restoration and Monitoring

In surface ecosystems, the restoration or maintenance of ecosystem functions, often measured as biodiversity, is a common goal — sometime a legal requirement — in environmental management. Many groups of animals are equally, even more, diverse in groundwater as in surface water (Rouch and Danielopol 1997, Sket 1999, Danielopol *et al.* 2000) so there is a strong argument to apply the same ultimate management goal to both surface and groundwaters. To achieve this goal, understanding of the composition, distribution and processes of aquifer ecosystems needs to improve substantially.

In addition to serving as the standard to which remedial work should strive, intact groundwater ecosystems have other attributes of potential interest to those involved in groundwater remediation. Firstly, they may have a functional role in the remediation process, particularly through their interaction with microbial communities (see below). Secondly, they can serve as sentinels of change in groundwater ecosystems. For example, heavy metals can present a risk for human health and the aquatic environment. Interstitial and hypogean macroinvertebrates bioaccumulate heavy metals from sediments in a manner very responsive to water fluxes and can be used as sensitive sentinels to trace heavy metal pollution in aquifers (Plenet *et al.* 1992). Groundwater fauna fit well with the sentinel system suggested by the Committee on Animals as Monitors of Environmental Hazards of the U.S. National Research Council (1991); they have a measurable response to the pollutants, they occur in the areas of the aquifer affected, the fauna is easily enumerated and sometimes the population size is adequate for sampling purposes. While the data were collected from the hyporheic zone the results can be extended to the aquifers (Plenet *et al.* 1992).

Stygofauna lack 'resting' stages so their presence is evidence of permanent groundwater. It can be inferred from this permanence and the distribution of obligate stygal lineages between continents, that some groundwater communities have existed throughout geological eras (Humphreys 2000, Poore and Humphreys 1998). Hence, the loss of these communities, or

elements of them, as a result of anthropogenic impacts would imply that the magnitude and/or rate of perturbation to these systems is greater than that experienced through these geological eras — sentinels indeed!

By focusing on the ecosystem, rather than the contaminant, there is scope for a range of circumstances in which the remediation of aquifer ecosystems may be unnecessary, even damaging. For example, remediation may destroy the halocline in salinity stratified waters and this is likely to disrupt anchialine ecosystems (Humphreys *et al.* 1999). Further, ecosystems dependent, for example, on sulphides of magmatic or petroleum origin for chemoautotrophic energy, or which are dependent on petrochemicals (see above), may not require remediation from some contaminants.

The status of groundwater — the level, direction and magnitude of flow — may have profound effects on the location and composition of subterranean populations (e.g. Rouch and Danielopol 1997, Watts and Humphreys in press). While these attributes could act synergistically with recognised contaminants, the attributes themselves can be contaminants when they fall outside normal variations as a result of anthropogenic agents. In which case, the physical status of groundwater may fall legitimately under the umbrella of remediation studies. The following trivial example suggests that these hydrological factors may result in profound change to stygal ecosystems and thus may be expected to influence the effects of contaminants (see also Gibert *et al.* 1994, Rouch and Danielopol 1997).

In the Australian arid zone, large spatial and temporal changes in water quality occur that result from the hydrogeochemical processes in the groundwater flow. Episodic rainfall, characteristic of the arid zone, may rapidly recharge calcrete aquifers causing the groundwater table to fluctuate widely, accompanied by large changes in salinity (Watts and Humphreys in press), and probably in oxygen. These changes may be expected to have important effects on biogeochemistry (Baker *et al.* 2000), as well as stygofauna.

CONCLUSIONS

The widespread occurrence of groundwater invertebrate faunas suggests that the target for remediation work should be to restore the diversity and functioning of the intact groundwater ecosystem. Indeed, such faunas may provide a sensitive indicator of presence of contaminant and success or otherwise of remediation. Under special circumstances there is the potential that remediation work itself could damage stygal ecosystems. Finally, it may be rewarding to investigate whether the endogenous communities of bacteria (Krumholz 2000) and macroinvertebrates (Sinton 1984) in groundwater can usefully be harnessed jointly to facilitate bioremediation.

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Bioavailability, Definition and Analytical Techniques for Assessment and Remediation of Contaminated (Inorganic and Organic) Soils

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ABSTRACT: Contaminated site remediation is often established on the basis of risk assessments that rely on both ecotoxicity and oral toxicity of contaminants of concern. The success of bioremediation, contaminated site rehabilitation and production of contaminant-free food is largely dependent on the bioavailability of the contaminants in the terrestrial environment. Currently, monitored natural attenuation (MNA) of toxic substances is seen as an attractive remediation option. In addition to natural attenuation processes, one assumption in MNA is that contaminant bioavailability in soils decreases with time (i.e. with ageing). Consequently bioavailability is used as the key indicator of potential risk that contaminants pose to both environmental and human health. However, the definition of 'bioavailability' and the concept on which it is based are unclear, the methods adopted vary throughout the world and, therefore, there is no single standard technique for the assessment of either plant availability of contaminants or their ecotoxicological impacts on soil biota. In this paper we define bioavailability as the fraction of the total contaminant in the interstitial water and soil particles that is available to receptor organisms with the extent of bioavailable fraction varying with time, the nature of soil types, organisms and environmental factors. Both bioindicators and geoindicators of bioavailable contaminant fractions are discussed.

KEYWORDS: bioavailability, metals, organics, bioindicators, risk, remediation

INTRODUCTION

The success of bioremediation, contaminated site rehabilitation and production of contaminant-free food is largely dependent on the bioavailability of the contaminants in the terrestrial environment. In general, microbial degradation of organic compounds is assumed to take place when the contaminant is present in the aqueous phase. Sorption, including ageing of soils, decreases contaminant bioavailability. Thus, bioavailability is considered as one of the key factors controlling the potential for either minimising or enhancing (a) contaminant uptake by crops, (b) adverse impact of contaminants on soil biota, (c) adverse impact of contaminants on human health and (d) the remediation of contaminated sites. However, the nature of contaminant species and soil types are also considered as essential factors influencing bioavailability.

Unfortunately, the term 'bioavailability' has been defined inadequately and used ambiguously in the literature with the concept on which it is based being unclear. Moreover, the methods adopted for measuring bioavailability vary throughout the world and therefore there is no single standard technique for the assessment of either plant availability of contaminants or their ecotoxicological impacts on soil biota. As a result, there is a need to review the work to define its definition, content and scope. Some of the difficulties probably arise because of confusion with the understanding of the bioavailability concept and relating this to the measurement of the contaminant availabilities. For example, a number of investigators relate bioavailability to that fraction of extractable contaminant that correlates with the total

contaminant uptake by plants. Although this has been quite successful with certain plants and soil types, its applicability has often been found to be fraught with limitations. Firstly, as bioavailability is often assessed by chemical extractions, it is likely that extractants may release those pools of contaminants that the plant roots and microorganisms do not exploit in the soil solution. This is supported by the definition that suggests that the concept of bioavailability is fundamental to toxicology and is not the same as bioavailable fraction that is largely a measure of solubility (Moore 2001). Secondly, and more importantly, the physiology of plants and microbes including the transport of metals across the membranes are often not considered during the assessment of contaminant bioavailability using the chemical extractants. The parameters that control the membrane transport of contaminants are species-specific and possibly dictate that the same bioavailable pool of contaminants in soils may not necessary result in the same rates of either plant uptake or impact on microorganisms.

This paper presents new evidence on: (a) metal-organic complex bioavailability to microbiota and plants (Krishnamurti *et al.* 2000); (b) time dependence of bioavailability (Naidu and Smith, unpublished); (c) contaminant accessibility as a key factor controlling bioavailability and remediation (Kantachote *et al.* 2000) and the influence of soil type on contaminant phytotoxicity to plants. The relationship between contaminant partition coefficient, bioavailability and LD_{50} of earthworms (Gupta *et al.* 2001) is also presented showing that soil type could play a significant role in controlling contaminant uptake by crops and also soil biota. Along with these, the paper demonstrates that powerful analytical techniques such as spectrometry, chromatography and atomic emission and absorption etc. fail to predict the biological effects or persistence of the contaminants (Megharaj *et al.* 2000). The integration of physicochemical and biological properties in the form of bioassays provide more accurate information about pollutant toxicity and biological availability, aiding successful bioremediation.

Definition of Bioavailability

Bioavailablity is defined as the fraction of the total contaminant in the interstitial water and soil particles that is available to the receptor organism. This suggests that there is a continuum between zero bioavailability and 100% bioavailability and within this spectrum the pool of contaminant available to receptor organisms may vary depending on the nature of organisms and the perturbations imposed by the environment.

There is however, a continued need to develop for soil ecosystems, a battery of toxicity tests with sensitive species. Considerable controversy exists in the literature related to what constitutes the bioavailable fraction, including the definition itself and the methods used for its measurements. For instance, microbiologists often regard the concentration that can induce a change either in morphology or physiology of the organism as the bioavailable fraction, plant scientists regard the plant available fraction as bioavailable fraction. Consequently, terms such as 'bioavailable', phytoavailable' and 'available' are in use. Thus there is no single adequate definition of bioavailability. Moreover chemists and plant scientists have often used a single chemical extraction as an index of bioavailability assuming that bioavailability is a static phenomenon while it may change with time.

Bioavailability of Contaminants in Relation to Bioremediation in Aged Soils

A clear link exists between biodegradation of toxic compounds, toxicity and bioavailability. The phenomenon of ageing (sequestration) in general results in the apparent decline of bioavailability associated with persistence and increased resistance of the contaminant

to extraction with solvents. For example, our laboratory studies (Ahmad *et al.* unpublished data) involving the possible bioremediation of long-term carbaryl contaminated soil have confirmed the reduced bioavailability of carbaryl in that soil. Inoculation of the long-term contaminated soil with carbaryl degrading bacteria showed approximately 45% of the carbaryl was apparently unavailable to the microorganisms. The amount of carbaryl degraded in this soil was related to the water extractable carbaryl content. This indicates the reduced bioavailability of contaminant in aged soils is a major constraint in the bioremediation. A similar effect of ageing on metal bioavailability and metal impact on soil biota has also been observed in our laboratory. Also, a similar effect of ageing on arsenic bioavailability has been demonstrated in our laboratory (R. Naidu and J. Smith, unpublished).

Toxicological Assays

Contaminant toxicity to microorganisms has often been regarded as a direct measure of bioavailability (Ronday *et al.* 1997). The advantage of toxicological bioassays lies in their ability to provide information about the synergistic interactions of two or more contaminants present as mixtures in soil, which can not be measured by chemical assays alone. A variety of toxicity tests involving microorganisms, animals and plants may be used with soil samples. However, much work needs to be done to assess the applicability of such tests to soils that are inherently heterogeneous, and contain a mixture of organic and inorganic pollutants and a variety of living organisms both eukaryotic and prokaryotic. To date, there is no ideal test suitable for heterogeneous chemical mixtures in soil and as such there is an urgent need for developing new assays or modifying the existing ones. The ideal toxicological assay should be simple to use, rapid, economical, sensitive, easily reproducible, amenable to statistical analysis, predictable, ecologically relevant and satisfactory from scientific and regulatory points of view. Most of the toxicity assays described in the literature have used freshly contaminated soils in which bioavailability of the contaminant may be much higher than the long-term contaminated soils, resulting in overestimation.

Algae have been shown to be sensitive to a wide range of contaminants including organics and metals. Algae were found to be more sensitive than either Daphnia, earthworm, Microtox, or root elongation (wheat and lettuce) bioassays to a range of chemical groups (organochlorine insecticides, herbicides and metals) tested from hazardous waste site (Miller *et al.* 1985).

Our research work on evaluation of toxicity in long-term total petroleum hydrocarbon (TPH)-and DDT-contaminated soils using chemical analysis, microbial biomass, soil enzymes (dehydrogenase, phosphatase, urease) and soil algae confirmed the inadequacy of chemical analysis for toxicological estimations and hence suggested the necessity of using chemical analysis in conjunction with bioassays (Megharaj *et al.* 2000a,b). Furthermore, changes in species composition of soil algae proved to be a more sensitive pollution indicator than other tested parameters. Algal growth inhibition tests using the aqueous elutriates obtained from TPH-contaminated soils showed that the water-soluble concentrations are more suitable to predict toxicity effects from contaminated soils.

In contrast to organics, bioavailability of a metal is a function of its speciation (Krishnamurti and Naidu 2000). Several studies showed that determination of total metal concentrations in soils does not reflect the bioavailability of the metal. In most cases the free ion form in the solution is the bioavailable fraction that is responsible for toxicity. For example hexavalent chromium, Cr (VI) is the most toxic form of Cr and conversion from Cr (VI) to Cr (III) is generally considered to be a detoxification step. Our recent work on toxicological evaluation of tannery waste contaminated soil using indigenous algae revealed that toxicity to algae is related to the presence of available Cr (VI) in that contaminated soils. Also, biodiversity

of the algae was greatly affected due to Cr contamination in this soil. These results were further strengthened by our work on other (Cd, Pb and Zn) metal-contaminated soils.

Soil Properties Influence Bioavailability in Different Soil Types

Often bioavailability tests are conducted by single soil tests irrespective of the soil types. Our recent studies using 7 different soil types, plant growth and soil microbiota studies revealed that contaminant partitioning between soil solution and solid phase dictates the bioavailability of contaminants and hence its toxicity. In general, an inverse relationship was recorded between the LD_{50} value and survival of earthworms in Cr(VI)-contaminated soils. A similar relationship was recorded from heavy metal phytotoxicity to plants. Our results demonstrate that critical total metal concentrations causing phytotoxicity to plants and soil biota varies significantly between soils. This is the first such result recorded in the literature.

Accessibility to Contaminants Bound to Soil Determines Biodegradation of Contaminants

Although bioremediation is considered to be one of the potential remediation options, the lack of DDT bioavailability due to its extremely low solubility makes it difficult to be a successful remediation option for long-term DDT contaminated soil. Several reports suggest the use of surfactants and cosolvents to increase the solubility of DDT. However, besides being expensive, the use of these chemicals can damage the soil. Hence, we examined the ability of sodium (Na) to increase DDT transformation as Na is known to cause clay dispersion and increase DOC content (dissolved organic carbon), thereby increasing the DDT bioavailability (Kantachote *et al.* 2000). Our work clearly demonstrated the increased solubility of DDT as shown by an increase in soil solution DDT concentration which is further supported by an increase in bacterial growth in the Na-amended, long-term DDT contaminated soil.

Indicators of Bioavailability

The main purpose of the use of bioindicators of pollution is to protect the biological health of the natural ecosystems by examining the pollution-induced changes in the living organisms. For this purpose, any organism that can be measured can be used as an indicator of that habitat. Currently there have been several organisms ranging from microbes to higher plants and animals that are being used as bioindicators. However, given the differences in the nature of pollutants, soils, the environmental variables, adaptability and resistance/tolerance of different organisms, it is not possible for any single species to fulfil all the requirements of a bioindicator. Hence it is necessary to have a battery of different organisms for pollution monitoring and as such only little is known in this direction. Considering this we have examined several biological parameters in assessing the impact of pollution in long-term DDT, petroleum hydrocarbon, pentachlorophenol and metal contaminated soils (Megharaj *et al.* 1988, 2000a,b). In long-term, DDT-contaminated soils microbial biomass carbon seemed to be a relatively less sensitive biological parameter than dehydrogenase activity or fungal population densities (Megharaj *et al.* 2000a). For instance, in this study there was >70% decrease in bacterial population in medium-level contaminated soil (27 mg DDTr kg^{-1}soil) over the low-level polluted soil (18 mg DDTr kg^{-1} soil) and yet there was a >30% increase in the total microbial biomass carbon in this soil (Fig.1). This was explained by the observed increase in fungal populations as the reason. Thus, microbial biomass carbon in this case may have been represented mainly by the pollutant-resistant organisms. Also this study showed an increased DDT toxicity to algal populations in high-level contaminated soil (34 mg

DDTr kg^{-1} soil). Of particular importance in this study was the decrease in biodiversity of algal population with the occurrence of only one algal species (*Chlorococcum* sp.) in high-level contaminated soil and elimination of nitrogen-fixing cyanobacteria.

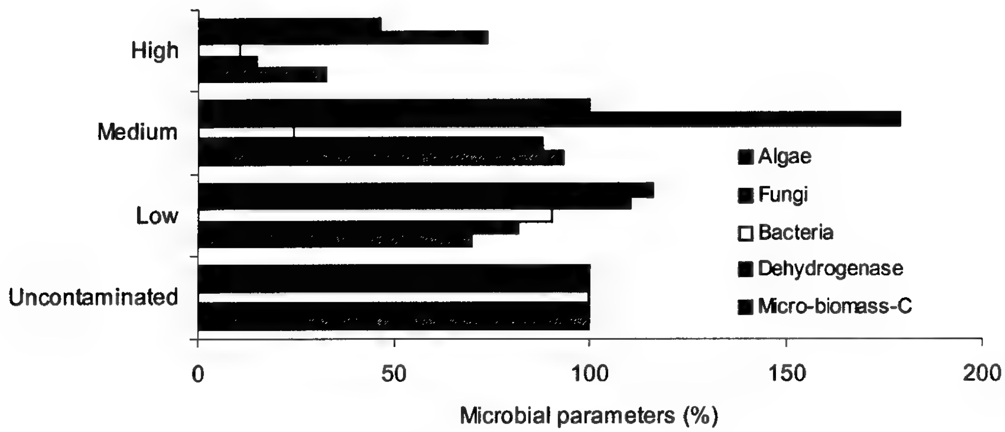

Fig. 1. Effect of DDT on soil biological parameters in a long-term contaminated soil

A similar trend was noticed in long-term total petroleum hydrocarbon (TPH)-contaminated soils (Megharaj *et al.* 2000b). In this study, depending on the TPH content, the polluted soils were classified as low (< 4000 mg TPH kg^{-1} soil), medium low (4000-8000 mg TPH kg^{-1} soil), medium (8000-12000 mg TPH kg^{-1} soil), medium high (12000-16000 mg TPH kg^{-1} soil) and high (>16000 mg TPH kg^{-1} soil). Microbial biomass carbon, soil enzymatic activities (dehydrogenase and urease) and algal populations decreased in all polluted soils with the decrease more pronounced in the soil with medium low-level pollution (Fig. 2). Of notable interest was the change in the species composition of algae in polluted soils with total disappearance of cyanobacteria in the medium low-level polluted soil. The total inhibition of algal growth by aqueous elutriate from medium low-level polluted soil confirms the observed toxicity of this soil to various biological parameters tested (Fig. 3). The fact that the medium low-level polluted soil contained a lower TPH compared to medium and medium high-polluted soils, yet showed higher toxicity than the latter soils, can not be explained by chemical analysis alone which points out the importance of the need to use chemical assays in conjunction with biological assays.

Photosynthetic microorganisms, such as microalgae and cyanobacteria, are ubiquitous in soils and their contribution to soil carbon, nitrogen and soil structure are well-known. Since microalgae resemble higher plants in terms of their cellular organisation, where as cyanobacteria are prokaryotes, use/development of bioassays with these organisms are valuable indicators of toxic effects to fundamentally different cells and hence better indicators of contaminant bioavailability as well. Thus, based on our research and available reports in the literature we suggest the use/analysis of algal (including cyanobacterial) populations in contaminated versus uncontaminated soils will be valuable indicators of pollution/bioavailability. However, the other parameters such as soil nutrients (especially N and P), soil pH and moisture content needs to be taken into account while using soil algae as pollution indicators.

As opposed to bioindicators, there is the possibility of identifying geoindicators, i.e. soil or geological factors that may provide indications of contaminant bioavailability. Given that the contaminant partition coefficient is a function of soil and environmental factors that control contaminant-soil interaction, work is in progress in our laboratory to assess whether the partition coefficient could be key indicator of contaminant bioavailability in soils.

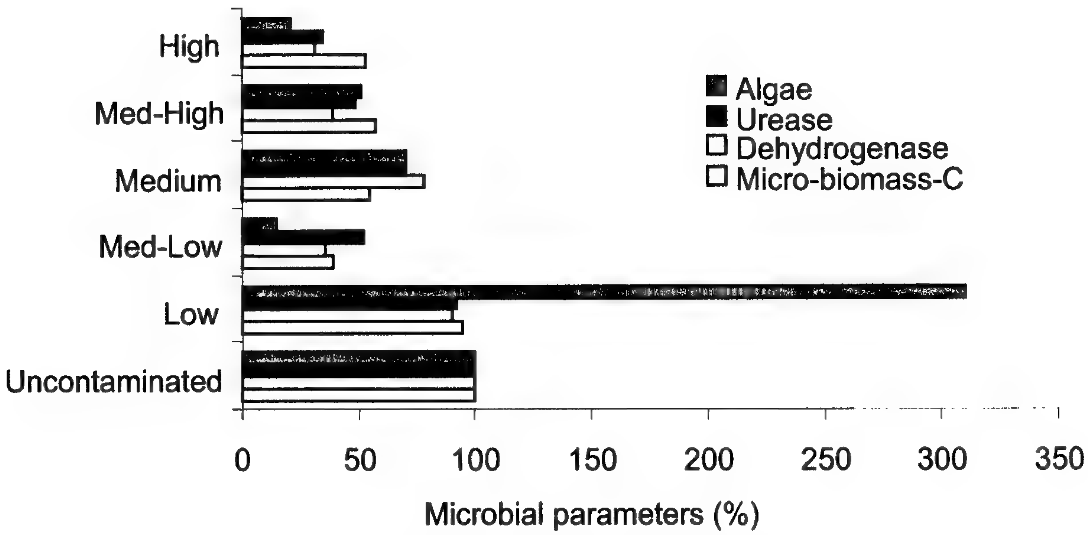

Fig. 2. Soil biological parameters in long-term TPH-contaminated soil

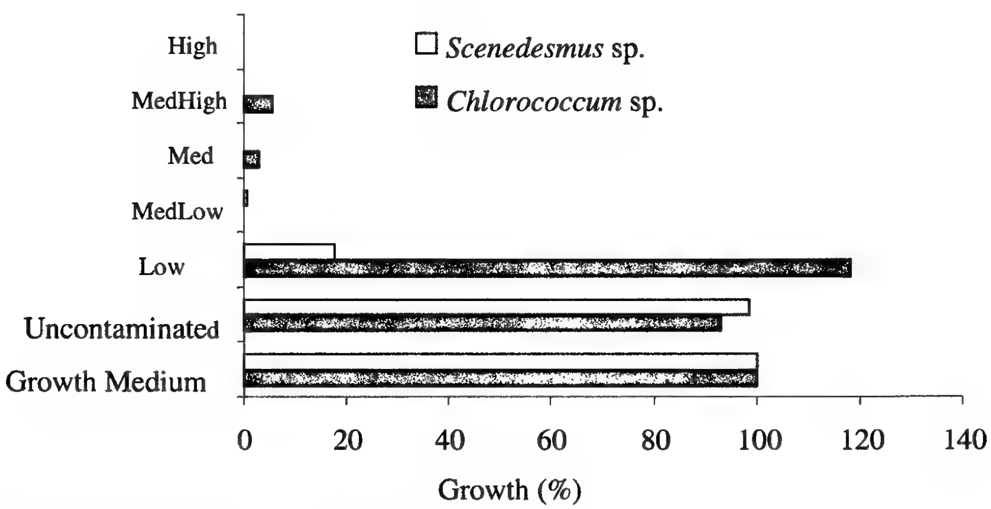

Fig. 3. Toxicity of TPH elutriates – algal bioassay

Does Ageing Enhance Natural Attenuation of Contaminated Soils?

Monitored natural attenuation of contaminated soils is now being considered as the eco-friendly technique of remediating contaminated sites. The basic assumption for such an approach is (a) the reduction in contaminant bioavailability with time and (b) adaptation by soil microbes to contaminants and (c) subsequent utilisation of contaminants (organics) as a carbon source. Our recent studies using long-term DDT-and arsenic-contaminated soils suggest that even after 10 years of field ageing, the bioavailability of both of these contaminants exceed the critical concentration that provides harsh conditions for microbe survival. This suggests that considerable caution must be exercised in assessing natural attenuation of soils. Work in our laboratory is now focussing on gut bioavailability of these contaminants and their potential availability to plants. Concepts being tested include the spill

over effect of the long-term bioavailability when contaminant loading exceeds the number of sites available for binding.

CONCLUSIONS

The need for development of suitable terrestrial bioassays (microbial) and the advantages and limitations of currently available bioassays together with the issue of definition of 'bioavailability' and its implications in bioremediation from a microbial point of view will be discussed. Based on the research conducted in our laboratory and elsewhere we suggest the following observations provide issues for future research:

(a) total concentration of a contaminant may not represent its bioavailability;
(b) pore water concentration is (though not always) a good measure of bioavailability;
(c) solid phase speciation must be considered during bioavailability assessments;
(d) algal bioassays are highly useful for bioavailability assessment;
(e) algal species composition seems to be a good biomarker of toxicity;
(f) terrestrial toxicological assays are under developed compared to their aquatic counterparts and there is an urgent need to develop suitable terrestrial toxicological assays;
(g) no single assay is adequate for toxicological analysis and a battery of assays comprising of different organisms is required;
(h) the potential role of partition coefficients as geoindicators of contaminant bioavailability needs consideration; and
(i) the effect of mixtures on contaminant bioavailability and resultant toxicity needs consideration in future bioavailability studies.

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Has a Remediation Technology Reduced the Bioavailability of DDT in Soil?

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ABSTRACT: Although remediation technologies may reduce contamination levels to what is considered appropriate by authorities, the real question still exists: has the remediated material become a lesser risk? Soil remediation guidelines in Australia currently stipulate targets or remediation end-points based on single total concentration values. This, however, does not assess the risk of remaining residues. Assessing biological availability of residues following remediation may be a more practical methodology for the determination of suitable remediation targets. Remediation targets must remain achievable and flexible to encourage cost-effective treatment. Assessing the biological availability of DDT in cattle dip soil demonstrated that only 3.5% (equivalent to 41.3μg bioavailable DDTr per g-soil) of the residues are available to biota. Following remediation of the soil using a chemical leaching process, the bioavailable fraction of DDTr increased to 47.8% (equivalent to 49.2μg bioavailable DDTr per g-soil). However, following composting of this leached soil, the bioavailable fraction decreased to 7.2% (equivalent to 3.1μg bioavailable DDTr per g-soil). A need clearly exists to assess bioavailability for determining suitable remediation targets.

KEYWORDS: assessment, risk, DDT, bioavailability, passive samplers

INTRODUCTION

Assessment of the environmental risk of a contaminant is a difficult, expensive and inaccurate science. The biological availability of the contaminant, however, is increasingly becoming a more important tool in assessing risks posed by contaminants in the environment. As the assessment of bioavailability is a powerful tool for the determination of environmental risk, the need to develop suitable methodologies for its determination is great (Tang *et al.* 1999). Traditional chemical extraction techniques analyse total contaminant concentration, but give no indication as to the bioavailability, hence risk of the contaminant in the environment. Environmental regulations as to permissible concentrations and remediation targets are based on single total concentration values. This is unlikely to correlate with environmental risk- a far more important issue than total concentration. The importance of including bioavailability as an exposure related parameter in the determination of environmental risk of a contaminant has been stressed (Feijtel *et al.* 1997).

Bioaccumulation is a very complex phenomenon and its measurement can be confounded by factors such as the structure, water solubility and molecular weight of the contaminant, and by the species, physical activity and physiological state of the test animal (Novak and Ahmad 1989). Consequently there is little understanding and accounting for the factors involved in the bioaccumulation of pesticides in animals.

The risk of chemical exposure to humans is also often overestimated by traditional chemical extraction procedures, and a need exists to better understand the bioavailability before setting appropriate risk standards (Bordelon *et al.* 2000). For example, dioxin

bioavailability to animals is significantly reduced where the contaminant has been in soil for some time (Bonaccorsi *et al.* 1984), and this should reflect appropriate permissible contamination levels to protect human health and the environment.

In this paper, we present a simple and reliable approach determining DDT bioavailability in soil. A semipermeable polymeric membrane containing fish oil passively mimicked the process of bioconcentration, thereby collecting pesticide residues available in the aqueous phase without changing their composition and releasing bound residues.

METHODS

Determination of Aqueous Bioavailability

Semipermeable polymeric membrane tubes were made from polyethylene lay-flat tubing, filled with 1.0 mL of cod liver oil. Soil (20.0 g wet weight) was weighed into 250-mL Schott bottles. The soil was mixed by gentle swirling with 100 mL of deionised water and 1 membrane was rolled and placed in each bottle. The bottle was sealed with a screw-top lid and then allowed to remain on the bench at 20 ± 3°C. Membranes were carefully removed from the bottles, and were washed thoroughly by running tap water. The membranes were wiped dry with paper towelling and then dialysed for 24 h in 100.0 mL of cyclohexane and an aliquot of the cyclohexane was diluted with *n*-hexane prior to gas chromatography.

Remediation of Soil

Soil (80 kg) was collected from a former cattle tick dip site in the Tweed Catchment in northeastern NSW. Vegetative material was removed from the sample and the soil was sieved to 2 mm and thoroughly homogenised. A portion of the soil was kept for residue analysis and tests for bioaccumulation potential. The remainder of the soil (70 kg) was remediated using a novel chemical leaching process. A portion of this remediated soil was kept for residue analysis and bioaccumulation potential, and the remainder (60 kg) was further treated using thermophilic composting for 6 weeks in a process described for contaminated sludges (Van Zwieten *et al.* 1997). The compost was analysed for DDTr (DDTr is the sum of DDT residues i.e. *o,p'*- and *p,p'*-DTT, DDD and DDE) concentration and bioaccumulation potential.

Experimental Design

For the determination of method variability, eight replicates for two contaminated soils per sampling time were prepared. Membranes were analysed for DDTr at day 5, 12, 19 and 26. Relative error was expressed as the absolute value of residuals from each model divided by the fitted values. The average of these was calculated for each metabolite and expressed as a percentage in Table 1.

To determine the changes to aqueous bioavailability following the implementation of a remediation technology, assessments were conducted on contaminated soil, contaminated soil following chemical remediation, and the composted remediated soil. Triplicate sets of sacrificial jars were allocated to each sampling time. The membranes were sampled at day 3, 7, 14 and 21.

RESULTS AND DISCUSSION

The passive samplers developed and applied in this project are a valuable tool for environmental assessment, and have been shown to have considerable potential for

quantifying the fraction of the soil contaminant that is available to biota. Using the passive samplers to assess contaminated soil will provide researchers, environmental regulators and site managers with the necessary information to accurately quantify the amount of a soil contaminant that is available to exert toxic effects or be accumulated in tissue and hence enter the food chain.

The bioavailability of a contaminant in soil or sediment can be influenced by many factors including the age of the residue, organic and clay content, and co-contamination by compounds such as surfactants. The semipermeable polymeric membranes contain fish oil and passively mimic the process of bioaccumulation. The membranes collect pesticide residues available in the aqueous (bioavailable) phase without releasing bound (unavailable) residues. A lipophilic compound (fat soluble) which is bioavailable is likely to bioaccumulate in animals.

For the semipermeable membranes taking up aqueous fractions of DDT and its breakdown products from cattle dip soils, the average relative error ranged from 4.3 to 20.3%. As shown in Table 1, membranes collecting low concentrations of DDTr had low absolute error but a higher relative error when compared to membranes accumulating greater quantities. The average relative error was calculated on the basis of three samples being used for experimental purposes. Further gains in precision from increased replication were shown to have little benefit in improving the precision of the methodology.

Table 1. Uptake of DDT and breakdown components ($\mu g\ g^{-1}$-soil) into semipermeable membranes. Values are averages for each component and soil type, standard deviation (sd), average relative error between two means based on three replicate samples.

	Day 5	Day 12	Day 19	Day 26	sd	Average Relative error (%)
o,p'-DDE Soil 1	0.039	0.048	0.053	0.065	0.010	16.2
o,p'-DDE Soil 2	0.545	0.597	0.629	0.687	0.057	5.6
p,p'-DDE Soil 1	0.927	1.106	1.208	1.254	0.124	8.4
p,p'-DDE Soil 2	32.479	33.006	34.405	35.153	2.053	4.3
o,p'-DDD Soil 1	1.194	1.431	1.597	1.674	0.143	6.8
o,p'-DDD Soil 2	0.509	0.554	0.582	0.592	0.052	5.9
p,p'-DDD Soil 1	0.536	0.614	0.668	0.835	0.061	6.4
p,p'-DDD Soil 2	0.167	0.186	0.206	0.215	0.025	9.6
o,p'-DDT Soil 1	8.252	10.130	11.152	11.296	1.223	8.2
o,p'-DDT Soil 2	2.984	3.290	3.457	3.479	0.860	19.5
p,p'-DDT Soil 1	6.764	8.083	9.148	9.617	1.032	8.5
p,p'-DDT Soil 2	1.912	2.212	2.279	2.337	0.549	20.3

The concentrations of DDTr in materials used for the bioaccumulation trials are presented on an ash weight basis to eliminate the potential bias created by dilution using composting (Table 2). In the composting process, incorporating organic matter with the treated soil deliberately changed the composition of the soil. This rehabilitation process was used to further degrade the organochlorine residues and to encourage the binding of these compounds to the organic fraction, rendering them less available to aqueous bioaccumulation. The total concentration of DDTr in the dip soil was 1174.3 $\mu g\ g^{-1}$, and following the chemical leaching process, 102.9 $\mu g\ g^{-1}$ remained. This leached soil was composted and after 6 weeks, only 43.2 $\mu g\ g^{-1}$ remained. The *p,p'*-DDE was further degraded from 71.5 $\mu g\ g^{-1}$ in the chemically leached soil to 23.2 $\mu g\ g^{-1}$ by the composting process. The composting also halved the concentrations of other DDT breakdown products, except for *o,p'*-DDT which was only marginally further degraded.

Table 2. Concentration of DDT and its metabolites in material used for bioaccumulation trials (presented on an ash weight basis to eliminate dilution influences). Each observation is a mean of 3 replicates.

Analyte	Dip soil $\mu g\ g^{-1} \pm \sigma^{n-1}$	Leached soil $\mu g\ g^{-1} \pm \sigma^{n-1}$	Leached and composted soil $\mu g\ g^{-1} \pm \sigma^{n-1}$
o,p'-DDE	>0.001	1.1 ± 0.2	0.4 ± 0.1
p,p'-DDE	17.3 ± 1.6	71.5 ± 3.5	23.2 ± 5.3
o,p'-DDD	20.9 ± 4.9	2.0 ± 0.5	0.6 ± 0.2
p,p'-DDD	9.0 ± 1.0	1.4 ± 0.3	0.1 ± 0.1
o,p'-DDT	604.5 ± 46.4	14.8 ± 2.4	12.8 ± 3.2
p,p'-DDT	522.6 ± 23.4	12.1 ± 2.9	6.1 ± 1.5
Total DDTr	1174.3	102.9	43.2

The accumulation of DDTr by membranes in cattle dip soil, following remediation using a chemical leaching process, and in this remediated soil following composting, is demonstrated in Fig. 1. Following 21 days of exposure, the membranes collected 41$\mu g\ g^{-1}$-soil from soil and 49$\mu g\ g^{-1}$-soil from remediated soil. The principal bioavailable component in the remediated soil was *p,p'*-DDE. In soil, 2.99 $\mu g\ g^{-1}$-soil of *p,p'*-DDE was bioavailable whilst in the remediated soil 37.52 $\mu g\ g^{-1}$-soil was bioavailable. The consequences of bioaccumulated DDE on egg-shell thinning is well established (Nygard 1999). This demonstrates the potential risks created in applying a remediation technology without assessing the bioavailability of remaining residues.

However, following composting of the remediated soil, there was a greatly reduced quantity of DDTr accumulated by the membranes. A maximum of 3.14$\mu g\ g^{-1}$-soil DDTr was available for uptake by the membrane after 21 days of exposure. The principal components found in the membrane were *p,p'*-DDE and *o,p'*-DDT.

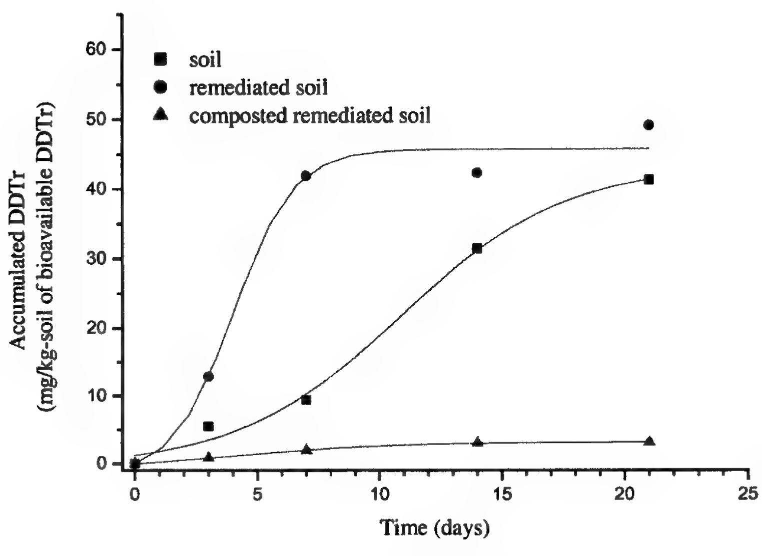

Fig. 1. Bioavailable DDTr in soil, remediated soil, and remediated soil following composting

The methodology presented here provides a powerful tool for determining the potential environmental risks associated with the implementation of a remediation technology, and in assessing the risks of bioavailability of contaminants in soil or sludge. It demonstrated that for

the leaching technology to be safely applied, composting of the material would be essential. Recent hypotheses stress the importance of setting reasonably achievable and practical remediation targets, rather than remediation end-points based on detection limit or nil-risk (LaGoy and Quirk 1994). The adoption of bioavailability assays will enable greater flexibility in assessing contamination risks, action levels and suitable remediation targets. The use of public monies for unnecessary remediation of contamination has been questioned (Proctor *et al.* 1998).

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Effect of Chrome-rich Tannery Wastes on Phospholipid Fatty Acid (PLFA) Patterns of Soil Microbial Communities

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ABSTRACT: Given the importance of microbial contributions to soil fertility and bioremediation, this work examined the effects of chrome-rich tannery waste on microbial populations as measured by phospholipid fatty acids (PLFAs), at different depths in the soil profile. Contaminated soils had increased pH, EC, organic carbon (OC), total Cr and hexavalent Cr [Cr (VI)] compared to uncontaminated soils. A significant amount of Cr (VI) was found in contaminated soils at all depths. PLFA analyses revealed that the concentration of fatty acids specific for bacteria was lower in contaminated soils compared to uncontaminated soils. However, 18:2ω6c, a signature fatty acid for fungi was higher in contaminated soil.

KEYWORDS: tannery wastes, chromium, phospholipid fatty acids

INTRODUCTION

Tanneries are one of the major industries that generate large quantities of organic-rich waste. Annually about 50000-60000 tonnes of solid and liquid wastes are disposed to land and water bodies. The disposal of these wastes is of great concern because of the high concentration of salt and chromium. The oxidised form of chromium, Cr (VI), is a potential respiratory carcinogen and therefore is of environmental concern (USEPA 1997). In long-term tannery waste-contaminated soils, there is potential for Cr oxidation and subsequent leaching to ground water (Naidu *et al.* 2000). Though reports exist on the effect of tannery waste on chemical characteristics of soil (James and Bartlett 1983, Makdisi 1991) only limited research has been performed regarding the long-term effect on microbial diversity.

Moreover, in order to formulate a sound bioremediation strategy for Cr-contaminated soils, it is necessary to determine the nature and diversity of microorganisms present. In this paper, changes in microbial populations due to long-term tannery waste contamination were determined by measuring the phospholipid fatty acid patterns in the soils (Steinberger *et al.* 1999). This widely used technique examines the changes in the total microbial community structure and hence could be used as an indicator of pollution (Zelles 1999). No report exists on the long-term effect of tannery wastes on microbial diversity and population of tannery waste-contaminated soils. The main objectives of this paper were to determine the long-term effect of tannery waste disposal on the microbial populations and diversity.

METHODS

Soils were collected from a long-term tannery waste-contaminated site at Mt. Barker, Adelaide, South Australia. One contaminated and an adjacent uncontaminated soil profile was chosen for the present study. Soil core samples were taken at five different depths (0-10, 10-

20, 20-30, 30-50 and 50-100 cm). Five replicate samples were taken at each depth, pooled and used for further studies.

Chemical Analyses

Soils were air dried and sieved (2 mm diameter). Soil pH and EC were measured in 1:5 soil water extracts after shaking in an end over end shaker (18 h, 10 rpm at 25°C). The extracts were filtered (0.45 μm) and total Cr and Cr (VI) were measured in soil solution. Total Cr in soil was also measured after digestion with aqua regia. Chromium was analysed by atomic absorption spectrophotometer whereas, Cr (VI) was analysed by ion chromatography, Method 7199 (USEPA 1996). Soil organic carbon content was measured by the wet oxidation method of Walkley and Black (Allison 1965).

PLFA Analyses

Field moist soils were extracted and analysed similar to the method of Bossio and Scow (1998). Soil (12 g) was extracted overnight with 75 mL of buffer containing a 1:2:0.8 ratio of chloroform, methanol and phosphate buffer (8.7 g L^{-1} K_2HPO_4; pH 7.4). The mixture was filtered and then extracted with 25 mL each of chloroform and phosphate buffer. The solvent phases were allowed to separate overnight then the chloroform layer was decanted and evaporated to dryness by rotary evaporation. The dried extract was dissolved in 3-5 mL of chloroform and phospholipids separated using a silicic acid column. Neutral fatty acids and glycolipids were eluted with 10 mL of chloroform and 20 mL acetone, respectively. The polar lipid fraction was eluted in 10 mL methanol, which was then dried under gentle stream of nitrogen. Polar lipids were subjected to overnight acid methanolysis (60°C) with 1.5 mL of methanolic H_2SO_4 (1% H_2SO_4 in methanol) and 100 μL of $C_{19:0}$ (nonadecanoic acid methyl ester) as internal standard. Fatty acid methyl esters (FAMEs) were then extracted with petroleum ether (2 x 5 mL) and dried under nitrogen. The dried extract was redissolved in 100 μL of hexane and analysed in a gas chromatograph equipped with flame ionisation detector using the MIS Eukary method (MIS, Microbial ID, US). Samples were run for 38 min with the temperature program ramped from 170°C to 250°C at 5°C min^{-1}. Flow rates of hydrogen, nitrogen and air were 30, 30 and 400 mL min^{-1} respectively. Individual FAMEs were identified using the peak naming table component of the microbial identification system and quantified using the $C_{19:0}$ internal standard and expressed as % weight.

Statistical Analysis

Statistical analyses were performed using GENSTAT 5 (4^{th} edition) from Lawes Agricultural Trust, Rothamsted, UK. Differences in PLFA concentration between contaminated and uncontaminated soils were tested by ANOVA.

RESULTS

Disposal of tannery wastes significantly changed the chemical characteristics of soils (Table 1). There was an increase in pH from 5.6-8.0, EC from 0.1-1.5 dS m^{-1} and organic carbon from 0.5-15 % in contaminated soils. All these parameters were significantly higher in contaminated soils at all depths. In contaminated soil, total Cr ranged from 0.8-11.2 % and soluble Cr in soil solution from 0.1-0.9 mg L^{-1}. This contrasted with much lower levels in the uncontaminated soils.

Of the total water-soluble Cr, more than 50% was present as Cr (VI). The amount of Cr (VI) was proportional to the amount of total Cr and soluble Cr in soil solution. The pH, organic carbon, total Cr, water soluble Cr and Cr (VI) decreased with depth except EC which increased with depth.

Table 1. Chemical characteristics of contaminated and uncontaminated soils

Soil details & Depth	pH	EC ($dS\ m^{-1}$)	OC (%)	Total Cr ($mg\ kg^{-1}$)	Water-soluble Cr ($mg\ L^{-1}$)	
					Total Cr	Cr (VI)
Contaminated						
0-10 cm	8.1	0.31	15.7	102000	0.92	0.54
10-20 cm	7.9	0.63	12.7	112000	0.69	0.71
20-30 cm	7.9	1.00	7.9	101000	0.62	0.57
30-50 cm	8.2	1.04	5.8	103000	0.23	0.21
50-100 cm	7.7	1.53	0.5	8000	0.10	0.05
Uncontaminated						
0-10 cm	6.0	0.05	1.6	11	0.01	0.01
10-20 cm	5.6	0.05	0.9	7	0.02	nd
20-30 cm	5.6	0.04	0.6	9	0.03	nd
30-50 cm	5.5	0.05	1.0	9	0.01	0.01
50-100 cm	5.7	0.03	0.4	14	0.06	nd

nd – not detected

PLFA studies suggested that there was a shift in microbial community structure as evidenced by principal component analyses (Fig. 1). The contaminated and uncontaminated soils clearly separated along the first axis, which accounted for 57.8% of the variation of all fatty acids. A decrease in concentration was observed in all the fatty acids characteristic for bacterial populations (Table 2). The largest decrease was found in fatty acid i16:0 (ratio 0.3) followed by i17:0, 15:0, a15:0 and i15:0, however, only a small decrease (10%) in bacterial population size was observed. Fungal populations increased in contaminated soil (ratio 5.2) as determined by 18:2ω6c, the signature fatty acid (Olsson *et al.* 1995).

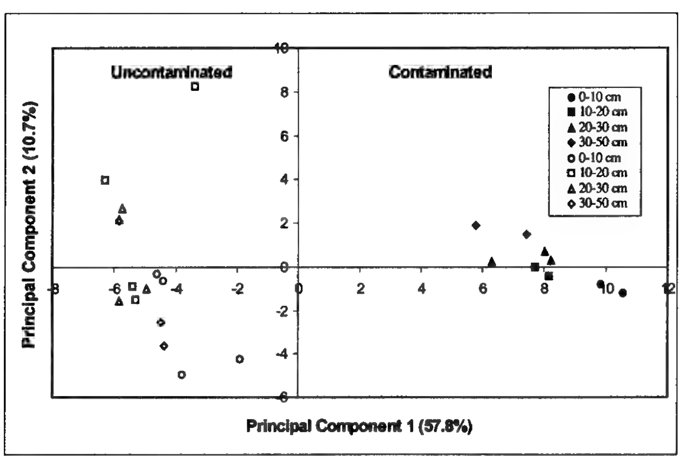

Fig. 1. Principal component analysis of PLFAs at different depths

Table 2. Concentration of phospholipid fatty acids in soils

PLFAs Wt (%)	Contaminated (C)	Uncontaminated (UC)	Ratio (C/ UC)
Bacterial			
i15:0	7.0	8.6	0.8
a15:0	4.2	6.0	0.7
15:0	0.8	1.1	0.7
i16:0	1.7	5.2	0.3
i17:0	1.8	2.9	0.6
a17:0	1.6	2.4	0.7
Total	17.1	26.2	3.8
Fungal			
18:2ω6c	0.8	0.2	5.2

DISCUSSION

Long term disposal of Cr-rich tannery waste to soils resulted in increased pH, OC and Cr status of the soil. Significantly higher concentrations of Cr were found to leach into soil solution, with more than 50% in Cr (VI) form. Chromium (VI) was also detected beyond 50 cm in the soil profile presumably due to leaching as a result of the alkaline nature of soil (Bartlett and James 1988). There is a potential threat at this site for groundwater contamination due to increased Cr (VI) concentrations higher than the maximum permissible level of 0.05 mg L^{-1} at all depths.

PLFA analyses revealed that there was a significant difference in PLFA patterns of contaminated soils when compared to uncontaminated soils. A marginal decrease in PLFAs characteristic of bacteria was observed in contaminated soil, which has also been reported in heavy metal-contaminated soils (Pennanen *et al.* 1996). An increase in fungal population (as indicated by 18:2ω6c) was also observed. This may be because of the decreased sensitivity of organisms to heavy metal contamination (Doelmann 1985) or would be related to higher levels of organic carbon in the contaminated soils.

CONCLUSIONS

This study showed that long-term contamination of soil with tannery wastes resulted in leaching of Cr (VI) deep into the soil profile. In spite of the high organic matter content of the soil, Cr (VI) was observed in soil solution at levels higher than the permissible limits. Bacterial PLFAs were highly sensitive to tannery contamination than fungal communities which may be mainly because of organic carbon content.

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Background Concentrations of Metals in Soils: Reconciling Fact with Fiction

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ABSTRACT: A prevalent belief in the environmental literature is that when concentrations of heavy metals in soils are found to be above 'background' levels, such concentrations must be the result of anthropogenic contamination. However, the validity of this concept is predicated on one crucial assumption, namely, that there exists a good understanding as to what constitutes background concentrations of metals in soils. At present, background concentrations of metals in soils are estimated by taking some measure (typically 95th percentile, mean or median) of metal concentrations observed in a regional or continental survey, comparing the values obtained to known average abundances of metals in the soil parent rock material, and accepting only those values which do not greatly exceed the parental abundances as reflecting the true (i.e. uncontaminated) background range. By definition, this somewhat arbitrary means for assessing background concentrations does not accommodate values that may be high due to natural variability. Background variation in metal concentrations, and the associated problem of mineralised but unpolluted soils, are recognised as limitations to the application of environmental investigation levels in the current Australian National Environmental Protection Measure. The principles of mineral exploration are founded on the recognition that element concentrations are variable and that very high concentrations do exist. Reconciling this fact with legislation that requires investigation and possibly remediation of soils if metal concentrations exceed a nominated value can pose serious challenges if the values have not been designed to account for this natural variability. We have identified stable geochemical indices that can be used to provide a better definition of background concentrations for As, Cr, Co, Cu, Ni, Pb and Zn in soils. By normalising surface versus subsurface metal concentrations, these geochemical indices can also assist in determining whether there have been recent inputs of these metals and metalloids to soils. Further research needs to be conducted to assess whether the indices can also reflect metal bioavailability in soils.

KEYWORDS: heavy metal, soil pollution, background concentration, baseline concentration, geochemical index

An Assessment of Arsenic in Groundwater at Cattle Tick Dip Sites

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ABSTRACT: A field study was conducted at dip sites in northern NSW to evaluate the potential for arsenic to move off site in groundwater. The distribution of arsenic in soil surrounding the sites was consistent with the past practices used to dispose of arsenic dip fluids i.e. pumping it out onto the soil surface. This indicates that the soil residues have not dissipated over a 50-year period. The As concentration in shallow (2 m) groundwater at contaminated clay-textured sites was below detection level of 1 $\mu g\ L^{-1}$. However, at sandy-textured sites, groundwater immediately adjacent to the dip bath contained significant levels of soluble arsenic. At these sites, the concentration of As in groundwater decreased sharply with distance (ca 20 m) from the bath, to less than 50 $\mu g\ L^{-1}$ (the ANZECC 1992 guideline for environmental waters). Qualitative assessment of As speciation in groundwater was made by ion exchange chromatography, and by theoretical assessment of the pH/Eh conditions of the soil. As (V) was the dominant species in most sites. As (III) was found in detectable quantities in groundwater at only one sandy site. Most dipsites in NSW are located on heavier textured soils rich in iron oxides. These sites pose a negligible risk of contaminating groundwater. However, a few dip sites also occur on coastal sand relics. These sites have potential to contaminate groundwater within small distances (i.e. to 20 m) from the dip bath.

KEYWORDS: arsenic, groundwater, speciation, leaching, piezometer

INTRODUCTION

Over the past century, NSW Agriculture has run a program aimed at eradicating cattle tick from the state. Cattle tick can transmit protozoal parasites that cause debilitating and fatal disease in cattle (tick fever). This costs farmers money in lost production, deaths and prevention measures. In that time the NSW government has built some 1600 dips for drenching cattle on NSW's north coast, and has used a wide range of tickicides, including arsenic.

Arsenic was first used in the control of cattle ticks in Queensland in 1895. Between then and 1955, arsenic (as the sodium salt of arsenous acid) was widely used on the NSW North Coast and along the Queensland border. This has resulted in soil contamination at dipsites typically in the range of several hundreds to several thousands of mg As kg^{-1}.

Contamination of soils surrounding dip bath is a consequence of the nature of the dipping process. Figure 1 gives a plan layout of a typical dip site. Cattle are plunged into the dip bath, causing the dipping fluid to splash from the bath to the soil. The cattle are then swum out of the bath, and held in a 'drip pen' for a short time before being released to holding yards. The retention period in the holding yards results in contamination of the soil within the yards.

Scooping of sludge, comprising soil, hair and faecal matter from the dip bath into a disposal pit, leading to the formation of a 'scooping mound' also resulted in contamination of surrounding soil, but this contamination is more localised. Additionally, the disposal method

for used dipping fluid was to pump out the dip onto the surrounding soil and recharge with a new or fresh chemical.

Encroachment by urban development into rural areas containing cattle dips has resulted in the need to assess the risk posed by arsenic contamination at these sites. This involves assessment of the type, amount, and mobility or bioavailability of residues at these sites and the development of strategies to manage risks associated with these residues.

Previous studies into As-contamination/mobility have relied on assessments of arsenic species present in the soil or sequential extraction methods to predict the risk of arsenic mobility. Speciation has been achieved theoretically, by means of soil redox assessments and comparison with standard phase diagrams. Sequential extraction techniques are indicators of potential mobility (Mclaren *et al.* 1998) and do not directly assess mobility. Both of these approaches have their limitations and caution should be exercised when interpreting them. Lindsay and Sadiq (1983) found that many redox related transformations were slow, and the products poorly defined. Gruebel *et al.* (1988) suggest that achieving even qualitative interpretation of data from sequential extraction techniques is exceedingly difficult.

This study was conducted to determine if there was any direct field evidence for arsenic movement in shallow groundwater from contaminated dip sites in northern NSW.

METHODS

Site Selection and Sampling

Six dip sites were selected from a GIS database of some 1600 sites in northern NSW. The database records site characteristics as well as history of chemical use. Site selection was based on a number of criteria, aiming at combinations of chemical use, soil and hydraulic properties considered to characterise worst case scenarios for As movement.

The first criterion was a high usage of arsenic. Dip sites with high cattle throughput, and a long history of arsenic usage will consequently have high arsenic inputs to the soil.

The soil and hydraulic properties of the site will determine the species and capacity for water movement. Sites chosen included sands, with high hydraulic conductivity, and low sorption capacity. Clay sites were chosen which had shallow watertables and/or high cross-site hydraulic gradients. These sites also had high iron oxide content and hence high As sorption capacity.

The third criterion for site selection was the soil redox state. Sites featuring high water tables or frequent inundation were chosen as the reducing conditions of these sites favours the formation of As (III) species, leading to increased As mobility.

The use of the carbamate tickicide Promacyl, since 1977 in some sites was also taken into account. This chemical is stabilised in the dipping fluid by addition of superphosphate. Phosphate in soils increases As leaching through competition for sorption sites in the soil (Manning and Goldberg 1996). Promacyl usage for each site is indicated in Table 1.

Transects of nested piezometers were installed at each site and are depicted in Fig. 1. Three piezometers were installed at each sampling point to depths of 1, 2 and 3 m, and screened over the lower 300 mm. Site 1 was installed with individual piezometers, where screen lengths of 1500 mm were used. An upslope, uncontaminated point was sampled at each site, to establish natural background As levels for that location.

Piezometers were installed in wells formed using a hydraulically-driven soil corer. Half-metre depth increments of cores obtained were homogenised and sub-sampled for As content. Fine sand was packed about the screen, then sealed above using bentonite. The well was backfilled with native soil and sealed at ground level with bentonite. Test wells at sites 2-

6 were developed by pumping out three well volumes, and a further one volume prior to each sampling. Site 1 was pumped out until stable oxidation/redox potential and pH readings were obtained, using in-line measurement.

Arsenic Determination

Soils

Samples were dried, milled and sieved to 2 mm, then sub-sampled and ground in a Retsch ball grinder. The 150-µm fraction was used for extraction. Samples were digested in nitric and hydrochloric acids by microwave digestion and analysed by AAS in accordance with NSW Agriculture method 275.001.

Water

All water samples were filtered on-site, through 0.45-µm membrane filters. Samples for total As were acidified with nitric acid, samples for speciation were not.

Total As in water was determined using graphite furnace, atomic absorption spectroscopy (NSW Agriculture 176.002) or ICP-AES (NSW Agriculture 170.004).

Speciation

Arsenic speciation was conducted on selected samples. Groundwater samples were collected into plastic containers with all air excluded. Care was taken to avoid aeration during sampling. Samples were cooled in insulated boxes with cold packs and transported immediately, to the laboratory where immediate analysis was undertaken. Separation of As species was achieved on an Allsep anion column (100 X 4.6 mm, 7 µm particle size) using All-Guard guard columns (Alltech Australia Cat. Nos. 51200 and 38109). The eluant was 0.025-M $NaHCO_3$ at pH 8.3 run at 1 mL^{-1} min. Eluant was collected in a fraction collector, and the appropriate fractions analysed by ICP-AAS.

RESULTS AND DISCUSSION

Soil arsenic distribution at the six sites studied was localised around the dip bath itself. Lateral soil contamination was mainly confined to 20 m from the dip bath (Fig. 1, Tables 1 and 2). The vertical distribution of arsenic at the clay sites was restricted to the 0-1.5 m layer (Table 2). There was a very defined boundary at depth between contaminated and non-contaminated soil, suggesting any vertical dispersive movement is extremely slow. The depth of contaminated soil is likely to have been the depth of wetting when the arsenic dip fluid was pumped out onto the soil surface.

The sandy sites were contaminated to a greater depth (0-2.5 m) than the clay sites. This contamination is more likely to be associated with vertical arsenic movement. There were soluble levels of As in piezometers immediately next to the dip bath that are of concern. Soluble arsenic was measurable in piezometers 10 and 20 m from the dip bath but at levels less than 50 µg L^{-1} (the ANZECC 1992 guideline for environmental waters). These sites are characterised by very high hydraulic conductivities, but a combination of low cross-site hydraulic gradient and some sorption to the soil has limited the spread of As residues

The groundwater pH and redox condition indicated that As (III) dominance was expected at site 3 only (Table 4). However, speciation measurements conducted by ion chromatography (IC) failed to show any of this species. The only As (III) detected using IC was at site 1, and then only traces were detected.

Sites 1 to 3 are all aeolian sand relics. The top 200-500 mm of soil at site 1 has been removed around the dip bath, and replaced with clay fill. The bath itself is on a slight ridge, with the water table about 2000 mm below the soil surface. The hydraulic gradient at this site was measured at less that 0.1%. Soluble As concentrations at this site were the highest encountered in this study. Speciation analysis revealed traces of As (III). These soluble residues were however, restricted to the immediate vicinity of the bath. The groundwater concentrations of test wells at 4 and 20 m downstream of the bath fell below the ANZECC guidelines.(ANZECC 1992).

Site 2 displayed less leaching and lateral movement than site one. This site is essentially flat, with only the dip bath itself built up slightly (this practice avoids inundation during wet periods). The water table at this site was typically 1700 mm below the soil surface, and again, had little gradient. Soil residues at this site were restricted to the vicinity of the dip bath, with low surface residues within the confines of the old draining yard. High soluble As was again detected immediately adjacent to the dip bath, but was not detected at 10 m.

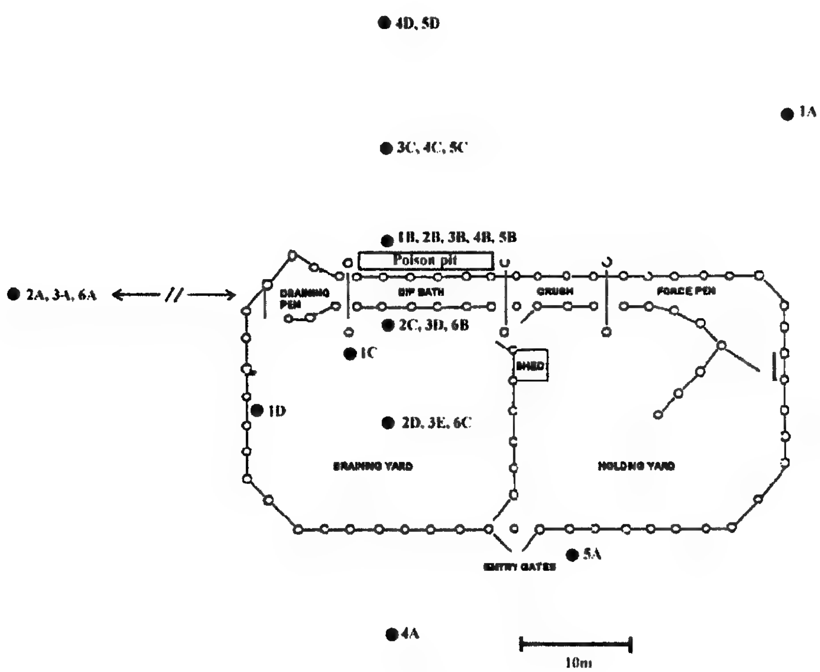

Fig. 1. Generalised dip site. Cattle are moved through the yards in an anticlockwise direction. The solid dots depict sampling points for the six dip sites studied. The codes on this figure correspond to codes given in Table 1 and 2.

Table 1. Soil textural properties of the dip sites in this study

Site	Soil profile properties
1	Red-brown clay fill to 0.2-0.5m around dip. Native soil medium sand with organic staining to 0.6m with some mottling 0.6 – 1.1m. No Promacyl used.
2	Sand texture to 3m. Organic staining to 0.5m underlain with fine yellow sand to 3m. Promacyl used.
3	Sand texture to 3m. Dark organic staining to 0.5m underlain with bleached sand to 3m. Some organic staining 2.5 – 3m. There is a dark cemented pan (coffee rock) at between 2 and 3 m below the surface. No Promacyl used.
4	Heavy clay soil with yellow mottling to 1m. From 1 to 2.5m heavy, iron enriched clay. Promacyl used.
5	Dark, organic, alluvial loam to 1m overlying heavy clay to 3m. Grey, bleached, reduced clay with red/yellow/grey mottling from 2.5m. Promacyl used.
6	Heavy brown clay to 1.5m Reduced brown/grey clay with massive structure from 1.5 to 3m. No Promacyl used.

Table 2. Total arsenic concentration in soil at the dip sites tested. (–) indicates no sample taken.

Site	Depth	A (background)	B	C	D	E
1	0-0.5m	4	Fill	Fill	6	-
1	0.5-1m	<1	Fill	Fill	<1	-
1	1-1.5m	4	191	11	1	-
1	1.5-2m	-	161	5	-	-
1	2-2.5m	-	265	-	-	-
2	0-0.5m	2	191	629	32	-
2	0.5-1m	1	29	42	1	-
2	1-1.5m	<1	7	81	<1	-
2	1.5-2m	<1	3	21	<1	-
2	2-2.5m	<1	13	33	<1	-
2	2.5-3m	2	4	38	<1	-
3	0-0.5m	4	27	<1	241	73
3	0.5-1m	2	8	<1	66	54
3	1-1.5m	3	3	<1	9	17
3	1.5-2m	<1	<1	<1	4	2
3	2-2.5m	<1	-	1	43	-
3	2.5-3m	-	-	<1	2	-
4	0-0.5m	4	88	4	5	-
4	0.5-1m	4	7	5	5	-
4	1-1.5m	10	7	3	7	-
4	1.5-2m	6	11	9	5	-
4	2-2.5m	1	12	11	4	-
4	2.5-3m	1	11	6	5	-
5	0-0.5m	8	205	12	4	-
5	0.5-1m	6	34	4	4	-
5	1-1.5m	6	11	6	5	-
5	1.5-2m	14	6	7	6	-
5	2-2.5m	6	11	1	2	-
5	2.5-3m	1	10	1	5	-
6	0-0.5m	21	103	15	-	-
6	0.5-1m	24	28	19	-	-
6	1-1.5m	8	101	13	-	-
6	1.5-2m	11	6	9	-	-
6	2-2.5m	6	4	9	-	-
6	2.5-3m	8	6	5	-	-

Site 3 featured a water table typically within 1m of the surface. The groundwater had low pH and low redox potential, this combination of factors is expected to enhance As (III) formation, and increase mobility. IC speciation of water samples taken at the site however, failed to detect this species. This is probably due to the very low levels of soluble As present at this site. Whilst elevated soil residues (17-73 mg kg^{-1}) were present 10 m from the dip, soluble As in groundwater was 18 ppb, well below the ANZECC guidelines.

The soil at sites 4 and 6 displayed high clay content and iron mottling, characteristics favouring strong sorption of arsenic. Residues exceeding background levels were restricted to the top 1000 to 1500 mm of soil depth. Site 6 was interesting in that it had the highest natural As concentration in soil. This site was located on the depositional zone of the Wilson's River flood plain.

Table 3. Arsenic Concentration in groundwater (mg L^{-1} filtered to 0.45μm)

Site/piezometer	A	B	C	D	E
1	<0.005	5.69	0.023	0.038	-
2	<0.001	0.001	1.32	<0.001	-
3	<0.001	0.086	0.015	0.087	0.018
4	<0.001	<0.001	<0.001	0.001	-
5	<0.001	<0.001	<0.001	<0.001	-
6	<0.001	<0.001	<0.001	<0.001	-

Table 4. The electrochemical properties of the groundwater at each site

Site	pH	Eh	pe	pe +pH
1	6.05	165	2.79	8.84
2	5.90	193	3.26	9.16
3	4.78	61	1.03	5.81
4	5.24	293	4.95	10.19
5	4.53	403	6.81	11.34
6	-	-	-	-

CONCLUSIONS

The results obtained in this study confirm that As residues remain at dip sites some 50 years after the last usage of arsenical tickicides. There was no field evidence indicating the contamination is moving off site in groundwater, which is indeed why these sites remain contaminated today. Lateral distribution of residues is consistent with the disposal methods of the day.

Some vertical arsenic mobility has been observed at very sandy textured sites. Lateral movement at these sites has been very limited due to the very low hydraulic gradients. The concentration of soluble arsenic at the boundaries of these sites were well below the ANZECC guidelines for environmental waters. These aeolian derived soils are confined mainly to the near coastal zone. A GIS analysis found there was a very small number of dip sites on aeolian landscapes in the region.

Given the fact that the residues have been present for the last 50 years or more, no immediate change to the status quo is expected. Continued maintenance of ground cover at these sites will be sufficient to limit surface movement of residues via erosion.

ACKNOWLEDGEMENTS

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Comparison of TPH (C6-C9) Concentrations Achieved by Two Detector Systems Using Purge and Trap Sampling

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ABSTRACT: This paper contains research conducted on detecting and quantifying volatile TPH from service station sites. The study was conducted to investigate if there were differences in TPH (C6-C9) concentrations determined by the use of purge and trap sampling technique with the use of GCMSD and GCFID. Contaminant free water was spiked with known amounts of unleaded petrol at four concentration levels, each as replicates of seven and analysed by the two detectors. The detectors were calibrated by using (a) BTEX mixture, (b) BTEX and octane mixture (c) octane and the TPH (C6-C9) concentrations obtained were statistically assessed to determine comparability. Comparison of results obtained using GCMSD and GCFID indicated that if octane was used as the calibration standard, the measured TPH (C6-C9) concentrations were comparable by the two detectors. However when either BTEX or a mixture of BTEX and octane was used as the calibration standards, the measured TPH (C6-C9) concentrations were statistically different.

KEYWORDS: TPH (C6-C9), BTEX, analysis, GCMSD, GCFID

INTRODUCTION

Petroleum hydrocarbons are chemicals containing both hydrogen and carbon atoms. Goldstein (1957) describes that the hydrocarbons include straight-chained, branched and cyclic alkanes, alkenes, monocyclic and polycyclic aromatic hydrocarbons. Analysis of petroleum hydrocarbons in soil and water is a primary environmental pollution testing parameter used to assess contaminated sites as described in Guidelines for Assessing Service Station Sites (NSW EPA 1994). The two fractions assessed are the volatile petroleum hydrocarbon fraction containing hydrocarbons ranging between C6 to C9 referred to as TPH (C6-C9) fraction and the semi-volatile fraction containing hydrocarbons ranging between C10 to C36 referred to as TPH (C10-C36). This study was conducted to obtain the concentrations of TPH (C6-C9) from water samples spiked with known amounts of the material and then analysed by two detectors. The current practice in Australia is to use both GCMSD and GCFID for the detection and quantification of TPH (C6-C9) by various laboratories based on based on methods in USEPA's publication SW846 (USEPA 1992). However when the results are examined and reviewed, it is frequently seen that there are substantial variations in the TPH (C6-C9) concentrations depending on the detector. The results of this study will assist in interpretation of the analytical data if two sub-samples from an original stock sample are tested by the two detectors.

METHODS

Reagents

Methanol (Merk-HPLC grade) and granular anhydrous sodium sulphate were used in the project. Millipore water further purified by passing through four cartridges of a milli-Q ultra cartridge system, was used in all purge and trap work. The solutions prepared for cleaning glassware included, chromic acid solution (prepared by saturating analytical grade potassium dichromate in analytical-grade concentrated sulphuric acid and adding 2% (V/V) water with caution) and Pyroneg powder (2%, W/V) in water prescribed for cleaning laboratory glassware.

Apparatus

Glassware used in experiments were treated by soaking overnight in a 2% Pyroneg solution, rinsed with water, soaked for two hours in a 2% chromic acid solution then washed with water, rinsed with acetone and air dried before use. If problems of contamination were encountered in glassware the cleaning procedure was repeated until the residues were removed. The glassware included 125-mL glass jars with screw cap lids and Teflon liners, 1-L glass jars with screw cap lids, glass rods with rounded edges, typically 6 mm diameter and 15 cm long. Purge and trap sampling vials (44 mL glass) and syringes (e.g. 25 μL, 500 μL) purchased from SGE and calibrated prior to measurements.

The soxhlet extraction apparatus for the extraction of TPH (C10-C36) fraction included soxhlet extractor tubes (70 mL) fitted with two-neck round-bottom flasks (500 mL), consisting of a second side neck with a thermometer probe inlet sealed by a Teflon-lined silicone septa. Whatman cellulose thimbles (25 mm ID 80 mm ID) used for extractioon of contaminated soils included were washed with DCM/acetone (1:1) prior to use for the soxhlet extraction. Glass volumetric flasks of various volumes and glass pipettes were calibrated prior to measurements. The samples with limited volumes were transferred into 200-µL glass with plastic collar GC vial inserts in place of the usual 2-mL GC vials.

Preparation of Samples and Standards

Preparation of standards for TPH (C6-C9) analysis

Stock solutions of standards were purchased and kept in a freezer at -20°C and prepared using procedures described in USEPA Method 8260A (1992). Stock solutions were only held up to the use by date and once the original ampoules were opened the solutions were stored in screw-top vials with minimum headspace at -20°C based on the storage stability study by La Greca (1996).

BTEX (benzene, toluene, ethylbenzene and xylenes) mixed standard was purchased (Supelco) at 2000 mg L^{-1} containing each benzene, toluene, ethylbenzene, o-, m- and p-xylenes. The n-alkane mixture of hexane, octane and decane was prepared at 5000 mg L^{-1} by using 99% pure standards and diluting them with methanol (50 mg of each hexane, octane and decane in 10 mL of methanol). The combined BTEX and C6, C8 and C10 (n-alkane standard mixture) were prepared by secondary dilutions as prescribed below. A secondary dilution calibration standard was prepared using 500 μL of the n-alkane standard mixture (5000 mg L^{-1} and 350 μL BTEX standard (2000 mg L^{-1}) in 25 mL of methanol in a volumetric flask. The solution was transferred to a septum-sealed screw-cap vial for storage at -20°C. This solution contained each n-alkane at a concentration of 100 mg L^{-1} and BTE and each of the Xs at 28 mg L^{-1}.

USEPA Method 8260 surrogate solution (Supelco) was purchased at 2000 mg L^{-1} each of dibromofluoromethane, d8-toluene and 4-bromofluorobenzene (Cat. 4-8959). The USEPA 8260 internal standard solution (Supelco) was purchased at 2000 mg L^{-1} each of pentafluorobenzene, difluorobenzene, d5-chlorobenzene and d4-1,4-dichlorobenzene (Cat 4-8958).

Gasoline range organic (GRO) check standard (Chemservice, Cat. TPH-4M) contained in a mixture of 2-methylpentane (1500 μg mL^{-1}), 2,2,4-trimethylpentane (1500 μg mL^{-1}), toluene (1500 μg mL^{-1}), 1,2,4-trimethylbenzene (1000 μg mL^{-1}), m-xylene (1000 μg mL^{-1}), o-xylene (1000 μg mL^{-1}), n-heptane (500 μg mL^{-1}), benzene (500μg mL^{-1}) and ethylbenzene (500 μg mL^{-1}).

Internal standards and surrogate solution were prepared using 250 μL of the stock 8260 surrogate solution and 500 μL of the stock 8260 internal standard solution added to 23 mL methanol in a 25 mL volumetric flask. The flask was made up to the mark with methanol and mixed and transferred to the instrument's standard vessel. This solution contained 40 mg L^{-1} of the internal standards and 20 mg L^{-1} of the surrogate standards. One microlitre of the internal standard and surrogate solution was automatically added to all samples by the OI auto sampler before the samples were purged.

Single level calibration standard solution was prepared by adding 40 μL of the secondary dilution calibration standard 100-mg L^{-1} n-alkane, and 28-mg L^{-1} BTEX secondary dilution standard into a 44-mL vial filled with organic-free water. This solution contained each n-alkane at approximately 91 μg L^{-1} and BTEX at approximately 26 μg L^{-1}. These standards were prepared fresh daily and used within 24 h of preparation.

Unleaded petrol spiking solution was prepared using 0.1 g of unleaded petrol weighed into a 100-mL volumetric flask (containing approximately 20 mL methanol). The flask was made up to the mark with methanol, capped and inverted three times to mix. This solution contained unleaded petrol at a concentration of 1000 mg L^{-1} in methanol.

GRO check standard was prepared by diluting GRO standard 1 in 10 in methanol and 20 μL of the mix was spiked into a volatile vial filled with milli-Q water to be used as a performance and standard check.

Apparatus for TPH (C6-C9) analysis

The major apparatus used for the TPH (C6-C9) analysis included a Hewlett Packard GC/MS 5890(II)/5972 coupled with an OI purge and trap. A Vocarb trap supplied by Supelco-Shimadzu for the trapping of purged volatile components was used. The GC was also equipped with an FID and two columns installed by using twin hole ferrule with one (column A) connected to MS and the other (column B) connected to FID. Both GC columns were Hewlett Packard HP-624, 0.25 mm x 1.8 μm. Column A (30 m length) was longer to compensate for the vacuum on the MS which decreased retention time relative to Column B (24 m length). The analysis was done in a split mode at 10 mL min^{-1}.

Preparation of samples for GCFID and GCMSD comparison

Samples were spiked at four concentration levels. The 'low level one' spikes were made by adding 10 μL of 1000-mg L^{-1} unleaded petrol standard into a 44-mL volatile vial containing milli-Q water. The vial was capped and inverted three times to homogenise.

The 'low level two' spikes were made up by adding 20 μL of 1000-mg L^{-1} unleaded petrol standard to 44-mL volatile vials containing milli-Q water. The vials were capped and inverted three times to homogenise.

The 'medium level' spikes study were made up by adding 100 μL of 1000-mg L^{-1} unleaded petrol standard to 44-mL volatile vials containing milli-Q water. The vials were capped and inverted three times to homogenise.

The 'high level' spikes were made by adding 200 μL of 1000-mg L^{-1} unleaded petrol standard to 44-mL volatile vial containing milli-Q water. The vials were capped and inverted three times to homogenise.

Seven replicates and seven blank samples without the unleaded petrol standard were prepared for each of the concentration levels.

Analysis of TPH (C6-C9)

GCMS Parameters: The conditions specified in the acquisition method for the analysis of TPH (C6-C9) were, Injector at 180°C, split vent flow 15 mL^{-1} min^{-1} at 140 kPa, column: HP-624, 0.25 mm I.D. with head pressure of 80 kPa during trap purge, program: 35°C for 4 min, ramp 10°C min to 250°C, hold for 2 min, pressure: initially 89 kPa constant flow, transfer line: 245°C, MS: full scan from 35 to 280 with threshold of 400 and A/D of 2. EMV 200 above autotune. MSD tuned using maximum sensitivity autotune, solvent delay 1.2 mins. OI Purge and Trap Parameters: OI purge and trap was programmed under the following parameters. Purge at 40 mL^{-1} min^{-1} for 8 mins, desorb at 245°C for 4 mins, and bake at 250°C for 8 mins. Transfer line and valve oven 100°C, MCS line temp 40°C.

The volume of water transferred from the sample to the sparge tube was set at 5 mL.

Calculation of BTEX concentration in samples

For each analyte identified in the sample, it was visually confirmed that the software has correctly identified the analytes. For diluted samples, the concentration was corrected as follows:

$$\textit{Conc. in original water sample} = \textit{Conc. in extract} \times \textit{dilution factor}$$

Where: Conc. in extract refers to the concentration calculated by the software package and dilution factor is the volume of the vial divided by the volume, v, of the original water sample taken (i.e. dilution factor = 44/v).

Calculation of C6-C9 TPH in samples

All peaks appearing in chromatograms of samples between retention times of hexane and decane were integrated using the Hewlett Packard chemstation software.

The internal standards and surrogates of the blank were integrated using the same software.

The response due to C6-C9 fractions was calculated by subtracting the total area of the internal standards and surrogates of the blank from all the peaks appearing in chromatograms of samples between retention times of hexane and decane.

The octane and BTEX peaks in the chromatogram of the standard were manually integrated. The area of each peak was determined manually.

The evaluated three standards were:

Octane only	51 ug L^{-1}
BTEX	152 ug L^{-1}
BTEX+Octane	203 ug L^{-1}

The concentration of the C6-C9 by GCMS in a sample was defined as follows:

$$\text{Conc. in Sample} = \frac{\text{Response of C6 - C9 fraction} \times \text{x } \mu\text{g/L}}{\text{Response of standard}}$$

The response due to C6-C9 fractions was calculated by subtracting the total area of the internal standards and surrogates of the blank from all the peaks appearing in chromatograms of samples between retention times of hexane and decane.

The response of standard was the manually integrated octane and BTEX peaks in the chromatogram of the standard.

The concentration (x) of the C6-C9 by GCFID was determined similar to the GCMSD using retention time as the identification tool.

Statistics and Measurement Uncertainty

The various statistical testing was based on Miller and Miller (1993).

A t-test was used to assess the statistically significance of difference in measured TPH (C6-C9) concentrations using different detection methods.

The error of the mean values obtained within a method was computed using the mean value, the standard deviation, the number of replicates (n) and the t-distribution value, t, obtained for a 95% confidence limit at a (n-1) degrees of freedom obtained from statistical tables.

$$\text{Error} = \pm t * \text{standard deviation} / \sqrt{n}.$$

Investigation of whether the means of two measured values are significantly different is applied to decide if the difference of concentrations obtained from two methods (Δ) exceeds the statistical uncertainty, U, were based on Farrant (1997). Therefore, if U >/= Δ then methods produce statistically similar concentrations for TPH (C6-C9). If $\Delta > U$ different analytical methods do not produce statistically similar concentrations.

RESULTS

Examination of GCFID Versus GCMSD Quantitation on the TPH (C6-C9) Result Using Purge and Trap Sampling

Calibration standards BTEX, octane and a mixture of BTEX and octane were used for the comparison of GCFID and GCMSD. The t-test statistics show that there was no significant difference (p=0.05) between the measured TPH (C6-C9) concentrations when octane was used as the calibration standard. However a significant difference is evident between the results obtained by the two detectors if either BTEX or BTEX and Octane were used as calibration mixtures. The results are given in Table 1. The histograms comparing the techniques are presented in Figs 1-3. These include the mean results and the error of the mean result.

Table 1. T-test results for TPH (C6-C9) analyses

Method/ Standard	REP1	REP2	REP3	REP4	REP5	REP6	REP 7	Mean	RSD %	t-Test (two tailed) p=0.05
GCMS BTEX+Octane	120	152	151	133	136	127	147	138	9	t=5.31 tcrit=2.17 t>tcrit null hypothesis rejected the difference between two results significant
GCFID BTEX +Octane	105	107	121	108	115	93	100	107	9	
GCMS BTEX	107	135	135	118	121	130	112	123	9	t=6.23 tcrit=2.26 t>tcrit null hypothesis rejected the difference between two results significant
GCFID BTEX	90	91	103	92	98	85	92	93	6	
GCMS Octane	226	290	286	255	257	248	208	253	12	t=1.92 tcrit=2.23 tcrit>t null hypothesis held the difference between two results not significant
GCFID Octane	223	228	256	229	244	198	213	227	8	

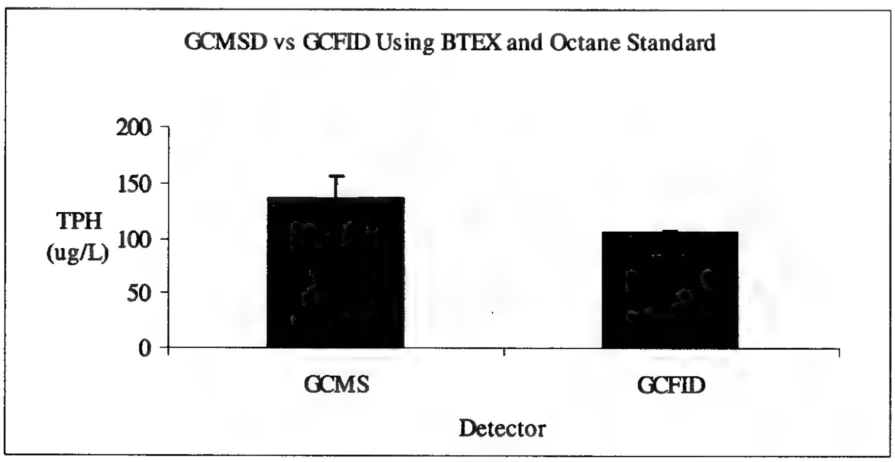

Fig. 1. GCMSD vs GCFIC using BTEX and octane standard

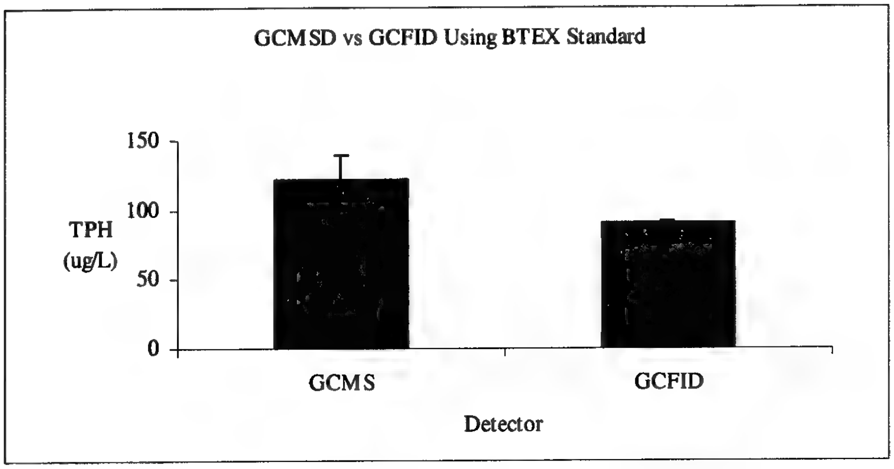

Fig. 2. GCMSD vs GCFID using BTEX standard

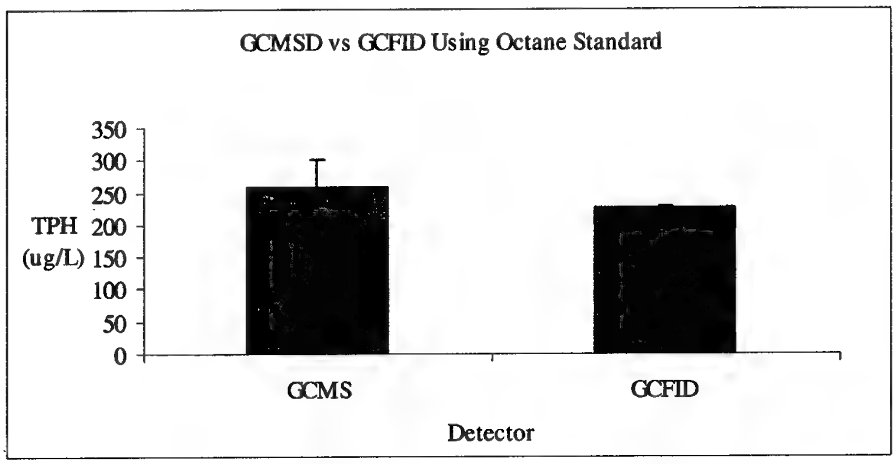

Fig. 3. GCMSD vs GCFID using octane standard

Table 2. Uncertainty (U) against the magnitude of the difference (Δ) of mean TPH (C10-C36) obtained by two detectors at p=0.05

Calibration Standards	GUFID VS GCMSD
BTEX+ Octane	Δ=31, U=12, Δ>U Not Comparable
BTEX	Δ=22, U=14, Δ>U Not comparable
Octane	Δ=25, U=28, Δ<U Comparable

DISCUSSION

Comparison of results obtained using GCFID and GCMSD for the analysis of TPH (C6-C9) is presented in Figs 1-3. This study included the split GCFID and GCMSD for the analysis and direct comparison of TPH (C6-C9) using BTEX, octane and BTEX/octane as standards. The statistical tests concluded that when BTEX or BTEX/octane were used as standards, the TPH (C6-C9) concentrations obtained by the two detectors were statistically different on a given sample. However, the statistical analysis of the results obtained when octane standard was used did not indicate significant differences between the TPH (C6-C9) concentrations.

CONCLUSIONS

Using octane as the calibration standard produced statistically comparable TPH (C6-C9) concentrations from GCFID and GCMSD techniques.

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Establishment of an Ultra-trace Measurement Facility at the Australian Government Analytical Laboratory

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ABSTRACT: A NATA accredited, ultra-trace level laboratory has been established as part of the Australian Government Analytical Laboratory in Sydney. The laboratory has the capacity to process up to 1000 samples per year for dioxins, furans and coplanar PCBs at the 1 $\mu g\ kg^{-1}$ (ppt) to 1 $ng\ kg^{-1}$ (ppq) level. Analytes are extracted and cleaned up using automated procedures wherever possible and quantitation is by high resolution gas chromatography with high resolution mass spectrometry.

KEYWORDS: dioxin, furan, PCB, trace, analysis, laboratory

INTRODUCTION

Following the dioxin and PCB contamination in Belgian chickens and animal products in April 1999, there was widespread demand for dioxin analysis both within Australia and overseas. Australia has little data that could be used to protect industry from spurious claims (either nationally or internationally) or to reassure the public that we do not have a widespread dioxin contamination problem.

It was realised that there was an urgent need for an ultra-trace laboratory to be established in Australia to measure background levels of dioxins, furans and PCBs in a variety of Australian samples. The targeted matrices include soils, waters, air, food, biota and biological samples. A decision was made, using a limited budget, to purchase the necessary equipment and to set up the laboratory at AGAL in Sydney where it compliments other established specialist facilities. These include the Australian Sports Drug Testing Laboratory (ASDTL), the Australian Forensic Drug Laboratory (AFDL) and part of the National Analytical Reference Laboratory (NARL).

BACKGROUND

Dioxins and Furans

Dioxins and furans are a family of chlorinated hydrocarbons (two hundred and ten have been identified) that can occur naturally during incineration of waste material and bush fires, and are also by-products of industrial processes (e.g. smelting, paper making, recycling). They are ubiquitous, lipophilic, persistent and accumulate in the food chain. The term dioxin and dioxins tend to be used interchangeably in both the press and in regulatory-type documents.

Whilst dioxins and furans show a wide variation in toxicity, studies have shown that there are seventeen dioxin and furan congeners (species) that exhibit the most toxicity. They contain four to six chlorine atoms with all the lateral positions (2,3,7, and 8) substituted. Toxic effects include dermal toxicity (chlor-acne), immuno-toxicity, reproductive effects and teratogenicity, endocrine disruption and carcinogenicity. The congener with the highest

toxicity is 2,3,7,8-tetrachlor-p-dioxin. Only three naturally occurring compounds have a higher toxicity (see Table 1).

Table 1. Comparative Toxicity of 2,3,7,8-TCDD (Wuest 2000)

Compound	Molecular weight	Lethal Human Dose ($\mu g\ kg^{-1}$)
Botulinus-Toxin A	900000	0.00003
Tetanus-Toxin	100000	0.0001
Diphtheria-Toxin	72000	0.3
2,3,7,8-TCDD	322	1
Curare	696	500
Strychnine	334	500
Sodium Cyanide	49	10000

Approximately 90% of human exposure to dioxins is estimated to occur through the diet, mainly from contaminated animal fat in the form of dairy products, breast milk, fat from meat, fish and poultry and eggs. Vegetables and cereals are also sources in some areas, e.g. adjacent to point sources of contamination such as smelters and incinerators.

Polychlorinated Biphenyls (PCBs)

Polychlorinated biphenyls are a group of compounds consisting of 209 isomers. The coplanar non-ortho substituted PCBs, the mono-ortho PCBs and the di-ortho PCBs are reported to have higher toxicity than the other congeners. It is therefore necessary to analyse PCBs on a congener-specific basis allowing these more toxic species to be accurately determined.

PCBs were widely used in appliances (starters for strip lighting) and in electronic components and in power transformers for their dielectric (insulating) properties. Indiscriminate and widespread dumping, combined with their resistance to biodegradation, has resulted in the accumulation of PCBs in the environment and in the food chain.

SAMPLE PREPARATION

Overview

Under normal conditions, the concentration of the PCDD/Fs in food, soil and ash samples is extremely low, typically in the picogram to femtogram range (10^{-12}g to 10^{-15}g). This compares to pesticide residue analysis where analyte concentrations are usually in the microgram to nanogram range. As a result, concentration factors of up to 6000 are often required for successful dioxin analysis. An effective and reproducible sample cleanup protocol is an integral part of dioxin analysis. Essential considerations for sample preparation are as follows:

(a) loss of compound due to adsorption on active surfaces such as glassware, separation columns and materials used for sample collection, clean up and analysis;

(b) cross contamination of glassware and sample handling equipment by use for both high level and a low level samples;

(c) solvents, glassware and materials used must be tested and free of dioxins to prevent contamination. Glassware used for dioxin analysis in fly ash or sewage sludge cannot be used for dioxin analysis in milk or food samples.

Starting with standard matrices such as fly ash, soil and food, a multi-step sample preparation and cleanup process is required to produce extracts suitable for GC/MS analysis. To validate the recovery of the extraction process and subsequent cleanup, a C^{13}-labelled internal standard mixture of $^{13}C_{12}$-2,3,7,8-dioxin and furan isomers is incorporated in to the sample prior to extraction.

Samples are freeze-dried if necessary (e.g. sludges, biota) and then Soxhlet extracted at elevated temperatures for eight hours or more using multi-channel, state of the art, hot, continuous solvent extractors.

Sample Purification

The raw extract has to be purified in order to be suitable for GC/MS analysis. Cleanup is achieved by liquid column chromatography using an automated, computer controlled, low pressure chromatographic system. Impurities are removed by sequential chromatography on disposable silica (acidic, basic and neutral) followed by alumina (acidic, basic and neutral) columns. Final cleanup is accomplished by washing onto a disposable carbon column. Reversing the flow on this final column and using selective solvent mixtures allows separate fractions to be collected for dioxins/furans, coplanar PCBs and non-coplanar PCBs. Solvent removal is accomplished by vacuum distillation and final concentration is completed by evaporation with a stream of purified nitrogen. There are several published and accredited methods for the analysis of PCDD/Fs - they include US EPA method numbers 23, 513/613, 8280, 8290 and TO9.

Due to the amount of care and aptitude required, it takes about 12 months to train a qualified analytical chemist to become proficient in the extraction and purification of samples for dioxin analysis at the parts per trillion level.

Analysis

Samples are initially screened using capillary gas chromatography and low resolution mass spectrometry in order to determine if there are high or trace levels of dioxins present. If high levels are found, appropriate dilutions are made before quantitation is accomplished by high resolution gas chromatography with high resolution mass spectrometry. HRMS, where masses are measured accurate to 4 decimal places (TCDD = 319.8965 amu) offers the high sensitivity and selectivity required to measure low levels of dioxins/furans/PCBs. The accurate mass measurement significantly reduces the possibility of undetected co-elution by interfering components or analyte mis-identification.

The HRMS method allows the analysis of one sample per hour. Once the calibration, resolution and sensitivity requirements of the instrument have been checked and certified to be within the method specifications, samples can be analysed together with blanks and certified reference materials. The maximum total sample throughput is about twelve samples per day. Data processing takes about one to two hours per sample (if the sample is positive). It takes at least six months to train a senior analyst to 'drive' a high resolution mass spectrometer.

COST

The major capital expenditure items involved in setting up the Australian Ultra Trace Laboratory are listed in Table 2.

Table 2. Major Cost Items for the Ultra Trace Laboratory

Item	Cost
HRGC/HRMS	\$500000
HRGC/LRMS	\$100000
Automated Sample Extract Purification System (2 channels)	\$75000
Multi-sample Evaporator	\$25000
Hot Soxhlet Extractor	\$20000
Certified Reference Materials	\$50000
C^{13} Surrogates and Standards	\$50000
Participation in International QC Programs	\$20000
Total	\$840000

In addition to these items, an air-conditioned, positive pressure, clean laboratory was proposed and built. The air conditioning was designed and fitted with Hep-A (0.2 μm) and carbon filters on both the inlet and outlet air to prevent any dioxin (both gaseous and particulate) from entering or leaving the laboratory. The positive pressure of air inside the laboratory and a twin door air-lock entry prevents outside air from entering at any time.

Other capital equipment items included two fume cupboards, a dishwasher, refrigerator, and various ancillary items of glassware and of course the costs of NATA accreditation.

In addition, expertise was sought from overseas laboratories with routine experience in dioxin analysis. Consultants were brought to Sydney to assist and advise in preparatory procedures for the extraction and cleanup trials, and arrangements were made for AGAL staff to visit overseas organisations in order that the expertise for the analyses could be assimilated as fast as possible.

CONCLUSIONS

As can be seen from the table of costs of essential capital items, an outlay of approximately \$1m is required and a lead time of twelve months is necessary before the first result for a dioxin/furan/PCB sample can be produced. These high costs and the expertise required in starting an ultra trace laboratory is reflected in the costs of analysis of a single sample, which can be up to \$2000.

ACKNOWLEDGEMENTS

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Advances in Dioxin Measurement Using High Performance Immunoassay Technology

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ABSTRACT: Immunoassay technology enables rapid screening of samples for dioxins. Results can be available within 24 hours, for a fraction of the cost of traditional methods. This technology can be used to screen samples prior to analysis by high resolution mass spectrometry and is critical in situations where large numbers of samples require rapid turnaround of results. Immunoassay uses a dioxin specific antibody molecule to detect and quantitate the dioxins present in a sample. The results are reported as toxic equivalent concentrations (TEQ). Immunoassay methods have been developed for soils, sediments, fly ash, oils and fish tissue.

KEYWORDS: dioxin, furan, PCDD/F, immunoassay, TEQ, toxic equivalent concentration

INTRODUCTION

Traditional dioxin analysis methods require complex sample preparation and cleanup procedures followed by analysis by high resolution mass spectrometry. Analysis can typically take 3 - 4 weeks and cost in the order of $1000 to $2000 for a single sample.

Immunoassay Technology enables screening of samples for dioxins in a relatively short time; typically results are available within 1 or 2 days and for a fraction of the cost.

This method can be used to screen samples prior to analysis by high resolution mass spectrometry and is critical in dioxin remediation projects where large numbers of samples require a fast turnaround of results.

METHOD

Immunoassay uses an antibody molecule to detect and quantitate the dioxins present in a sample. The antibody molecules, developed to be specific for dioxins are added at a predefined concentration. Two linked reactions form the basis of this type of test - the capture by the antibody of an enzyme labeled dioxin fragment and the inhibition of that capture by the analyte molecules in the sample. The unbound competitor enzyme is washed away, leaving an amount of bound enzyme inversely proportional to the level of poly chlorinated dibenzo dioxins and furans (PCDD/Fs). The colourless substrate is converted to a blue colour in proportion to the amount of bound enzyme. This is read and quantitated using a photometer and the results are reported as toxic equivalent concentrations (TEQ).

Structural Basis of Antibody Specificity

The basis of all immunoassays is the specificity of an antibody molecule for a particular chemical structure. Figure 1 depicts the binding site of an antibody, which has a structure

complementary to the target analyte. The noncovalent binding of the target analyte to the antibody's binding site occurs because of the lock and key fit between these complementary structures.

Molecules, which differ slightly from the target structure, may also bind to the antibody, though less tightly than the target analyte. Molecules, which differ greatly from the target structure, will not bind to the antibody.

Key concept: lock and key fit between analyte molecule and antibody binding site.

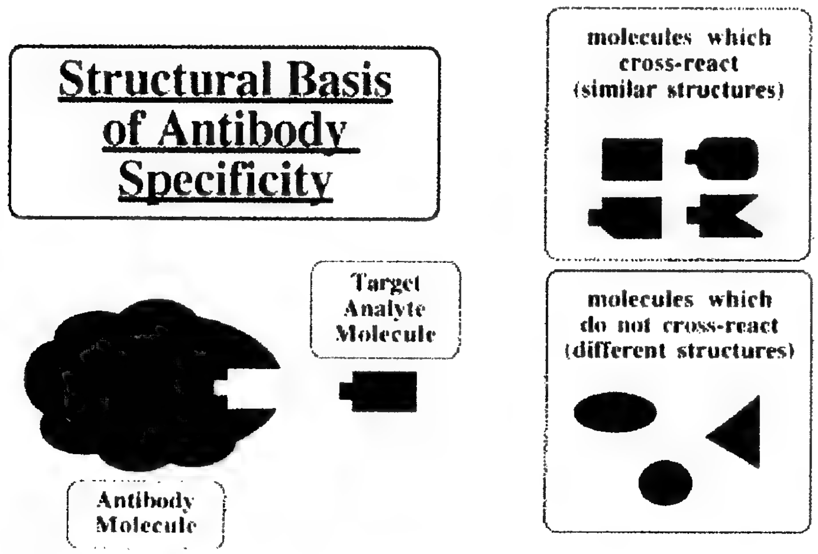

Fig. 1. Schematic of the structural basis of antibody specificity

Conceptual Basis of Competitive Enzyme Immunoassay

Two linked reactions form the basis of this type of test - the capture by the antibody of an enzyme labelled dioxin fragment and the inhibition of that capture by analyte molecules in the sample.

The baseline binding of the dioxin-enzyme conjugate to the antibody is affected by both concentration and cross reactivity of analyte.

When analyte molecules occupy dioxin-specific binding sites on the antibody, fewer sites are available to capture the dioxin-enzyme conjugate.

Cross reactivity, the ability of an analyte molecule to bind to the antibody, decreases as the structural similarity to the target analyte decreases.

Key concept: Test response is by competitive inhibition and is strongest for analyte structures that are most similar to the target.

Schematic Diagram of DF1 Dioxin/Furan Immunoassay Protocol

The schematic diagram shown in Fig. 2 illustrates and explains the incubation and wash steps of the immunoassay protocol.

Key concept: As the analyte concentration increases, colour development decreases.

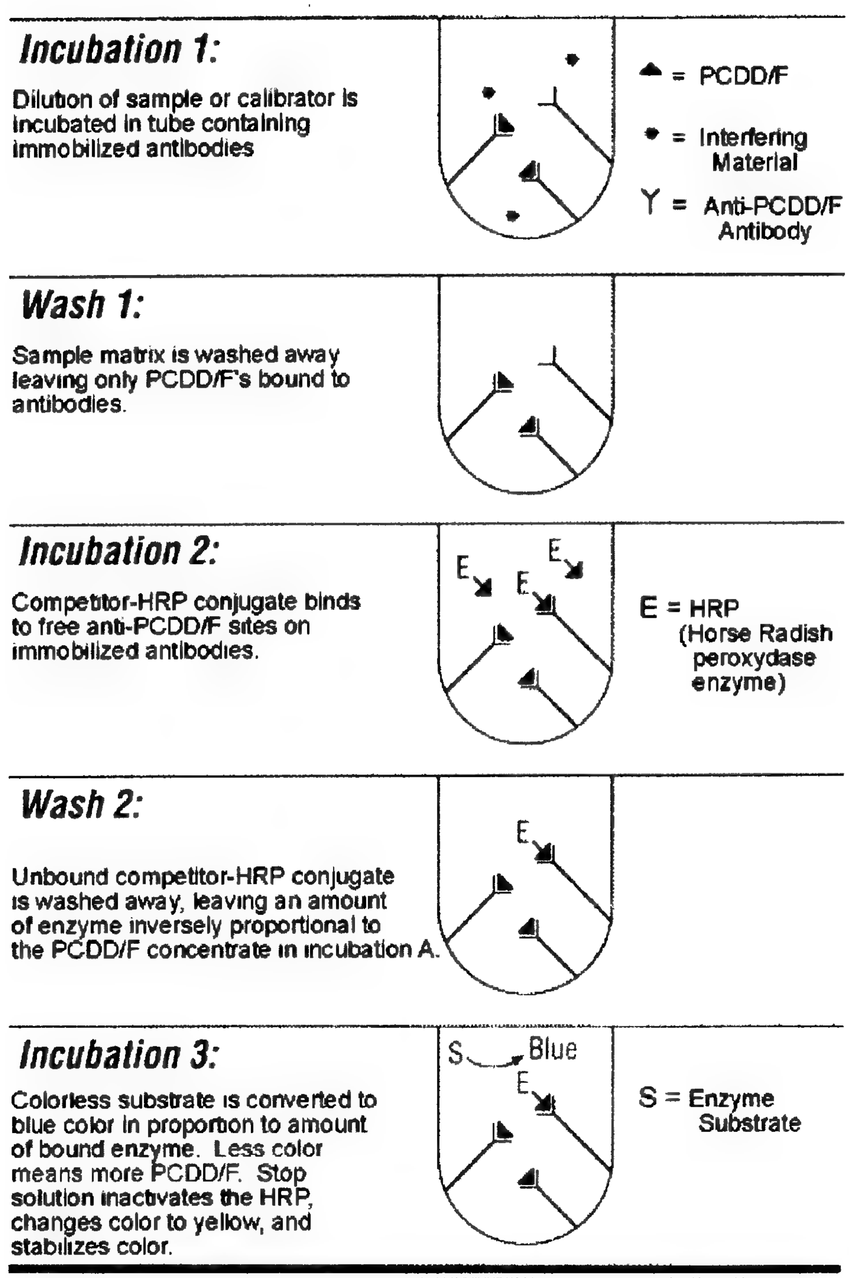

Fig. 2. Schematic diagram of test for polychlorinated dibenzodioxins/furans (PCDD/Fs)

Validation Data Supporting this Method – Soil Samples

Eighteen soil samples were analysed by conventional GC-MS and subsamples were extracted separately and analysed by immunoassay. Fig. 3 shows the correlation between immunoassay analysis and TEQ as determined by high resolution gas chromatography-high resolution mass spectrometry (HRGC-HRMS). The calculated regression line is shown with 99% confidence limits.

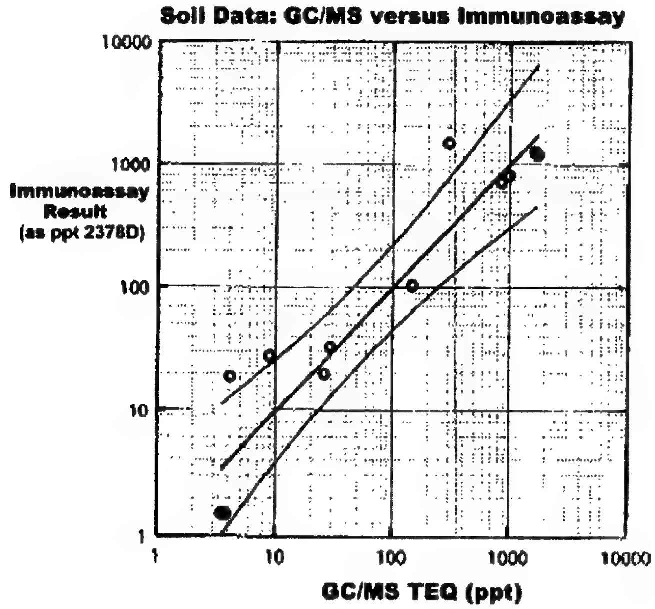

Fig. 3. Soil data: GC/MS versus immunoassay

The immunoassay results were also plotted in screening format (Fig. 4), indicating the TEQ value chosen as a screening level (10 ppb vertical line) and the immunoassay response at which the screening decision would be made (6 ppb horizontal line). The number of results in each quadrant is indicated on the plot.

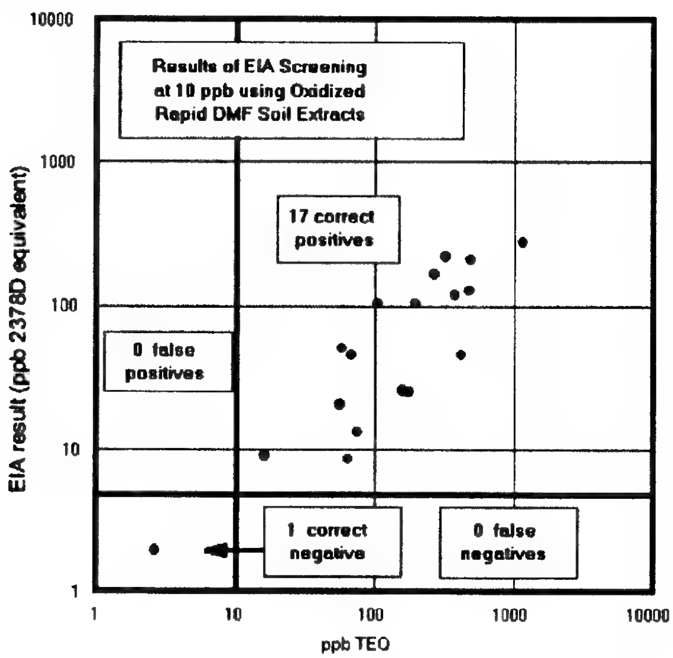

Fig. 4. Results of EIA screening at 10 ppb using oxidised rapid DMF soil extracts

Validation Data Supporting this Method – Ash Samples

Nineteen Incinerator fly ash samples were analysed by conventional HRGC-HRMS. Subsamples were extracted and analysed by immunoassay. Figure 5 shows the correlation

between immunoassay analysis and TEQ as determined by high resolution gas chromatography-high resolution mass spectrometry (HRGC-HRMS). The calculated regression line is shown with 99% confidence limits.

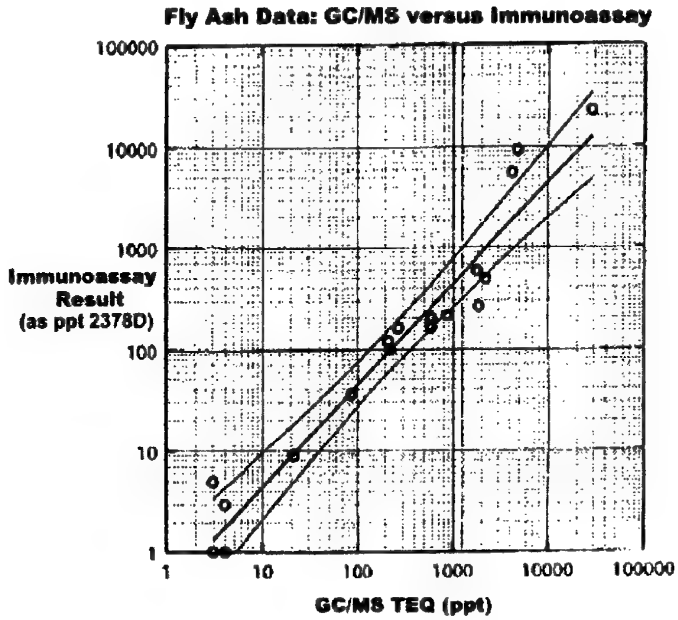

Fig. 5. Fly ash data: GC/MS versus immunoassay

The immunoassay results were also plotted in screening format indicating the TEQ value chosen as a screening level (10 ppt vertical line) and the immunoassay response at which the screening decision would be made (8 ppt horizontal line). The number of results in each quadrant is indicated in Fig. 6.

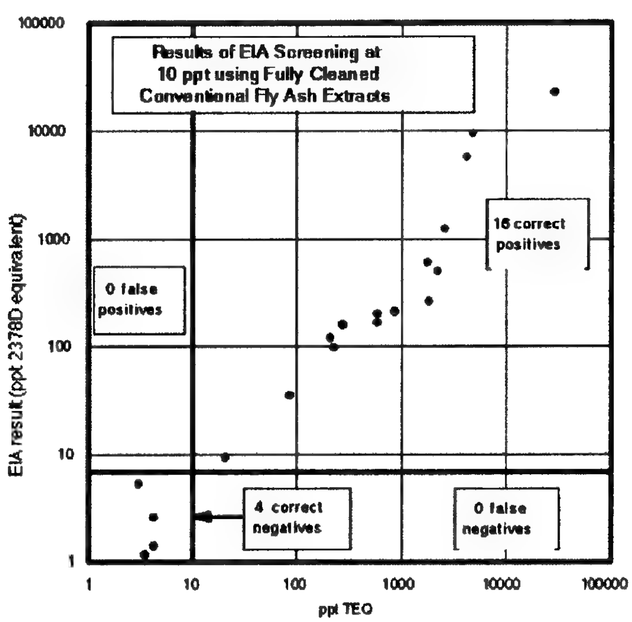

Fig. 6. Results of EIA screening at 10 ppt using fully cleaned conventional fly ash extracts

DISCUSSION

These results clearly establish the ability of the CAPE Technologies high performance dioxin/furan immunoassay procedures to analyse and report toxic equivalent concentrations (TEQ) in soil samples at parts per billion levels and fly ash samples down to low part per trillion levels.

Immunoassay methods have been developed for soils, sediments, fly ash, oils and fish tissue but it is possible to validate the immunoassay method for a range of other matrices.

CONCLUSIONS

Immunoassay technology enables sensitive, accurate, rapid and low cost screening of samples for dioxins. Results can be available within 24 hours, for a fraction of the cost of traditional methods.

This technology can be used to screen samples prior to analysis by high resolution mass spectrometry and is very useful in situations or projects where large numbers of samples require rapid turnaround of results.

The method and equipment is ideally suited to be set up and operated in a field or on-site situation.

ACKNOWLEDGEMENTS

Thanks to Stephen Grist who assisted with the preparation of the Poster Display.

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.....When Your Number's Up!

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ABSTRACT: It is a strange but sad reflection of the current state of the industry, that many of the proponents of the field of environmental science have never actually set foot in a commercial laboratory. Even those who have, often have little idea of the workings of the place upon which they rely for their data, data upon which they will lay exposed their reputations in the form of a signed report to a client. This paper explores some of the pitfalls waiting for the unwary, and encourages a greater dialogue and understanding between laboratories and those who use their services.

KEYWORDS: laboratory, analysis, assessments, guidelines, RPD

INTRODUCTION

"Take interest, I implore you, in the sacred dwellings which one designates by the expressive term 'laboratory'. Demand that they be multiplied and advanced. These are the temples of the future; temples of knowledge, wellbeing and happiness. There it is that humanity grows: greater; stronger; better."

Louis Pasteur (1822 - 1895).

It is a strange but sad reflection of the current state of the industry, that many of the proponents of the field of environmental science have never actually set foot in a commercial laboratory. Sadder still that even those who have, often have little idea of the workings of the place upon which they rely for their data, data upon which they will lay exposed their reputations in the form of a signed report to a client. Imagine the scenario: you are called as the expert witness in environmental litigation. You signed the consultants' report; you stand before the bench; and you swear that the report is an accurate reflection of the environmental condition as you understand it..... *but do you understand it?*

As an analytical chemist with almost twenty years of experience slaving over a hot Bunsen burner, I now find myself working as an environmental consultant. Allow me, therefore, to proffer my view as the laboratories' man ...in the consultant's court.

THE FRAMEWORK IN WHICH WE WORK

We live in a world where mathematics has taken a back seat to arithmetic, where cash-flow has replaced economics and where the words "guideline", "standard" and "benchmark" seem to have been re-defined by some regulatory bodies to mean "limit". ANZECC, NH&MRC, The Dutch Department of Spatial Planning and Environment, the USEPA and others all produce lists of environmental 'numbers' **(the numbers)**. Other **numbers** we may have to deal with have come from NATA registered laboratories who analyse our samples. The **numbers** must be sought after, achieved, or perhaps obtained by remedial works. The **numbers** are the very things upon which our reports depend, for without them we would have no basis for the evaluation of a site.

Environmental auditors are often bound by the **numbers**, frequently against their professional judgment, because in a court of law it may be that it is the **numbers** and not their professional judgment which will hold sway. So what, then, is the problem with the **numbers.**

THE NUMBERS, ...AND WHERE THEY COME FROM

Let us for a moment look closely at just one of the **numbers.** The ANZECC/NHMRC *Guidelines for the Assessment and Management of Contaminated Sites* (1992) give an Environmental Investigation level for zinc of 200 mg kg^{-1} in soil. If you send your soil sample to your normal laboratory of choice, and they send back that dreaded 201, what *does* it mean? The less critical amongst us would have the clients believe that 199=***good,*** 201=***bad!*** But what of **the numbers** from the lab, and how are they derived?

LETS LOOK AT THE PROCESS INVOLVED

The sampling and analytical process may be considered as a series of sequential steps leading to production of a NATA stamped laboratory report which will form the basis (and usually an appendix) of a consultant's report to a client.

Soil sampling

Soil sampling methodology has been pretty much defined by various guideline publications by such imposing organisations as the National Environment Protection Council and Australian Standards amongst others. All self-respecting environmental scientists plan their sampling process meticulously. They will either sample on a generic grid or target samples at where contamination is suspected to have occurred. They will obtain their soil samples in accordance with sampling procedures which include:

(a) equipment rinsate blanks;
(b) transportation blanks;
(c) multiple equipment washes in phosphate free detergents;
(d) the wearing of disposable gloves; and
(e) a myriad of similar sample cross-contamination protection measures.

However, most consultants seem to send their samples to the laboratory in a small glass jar with a tight fitting screw cap (say 200-500 g, few of us send any more than 500 g). Just how representative is that sample, and is it possible that the sample results are often more skewed by the sampling technique than by any subsequent part of the analysis process? You bet it is! If a sample taken from the field is not truly representative of the soils around it, how can any subsequent analytical results possibly be correct?

Soil scientists will tell you that a 'typical' soil (if there is such a thing) can have up to 25% stone content (stones being inert solids greater than 2 mm in size). Did you include even one stone in your 'representative' jar of sample? Be honest now. Many consulting environmental scientists, (and I have watched a few), deliberately **avoid** taking stones. They will even go so far as to remove larger ones from the sample jar if they mange to inadvertently get in there. Besides, if the sample container is a small jar, a large stone wouldn't fit in the first place. Hence, if your soil in the field has, say 25% stone content, and that stone is fairly inert in nature (say basalt or sandstone) your reported **number** from the lab will only represent

the possibly non-inert fraction and hence may be 133% of the actual metal concentration in the whole soil.

If you are sampling into basalt clays with small cobbles and floaters or river bed samples you could easily be excluding 90% of the true sample in favour of unrepresentative 'fines' hence skewing the results much more than any laboratory error ever could.

It is time that we re-thought our sampling processes and delivered, say, a 5 kg whole sample to the lab. That might be a bit more representative of the real thing. It would certainly give us a basis for claiming that we had a sample which might not suffer the extremes of subjective sampling technique. We could then ask the lab to prepare that whole sample, homogenise and extract a truly representative fraction for analysis.

There are those who would argue that the stones are irrelevant, that human or environmental health risk is based upon the contact with the fines. Equally there are others who would point out the potential costs of consigning stones to a secure landfill. Clearly there are field decisions to be made, but de we actually ***make*** them, or do we simply accept a default position of randomly stone-reduced sampling.

As to those careful cross-contamination avoidance measures; if we take 5kg rather than 250g, any potential serious impact from inadvertent sample cross-contamination drops massively. By taking such a small sample we risk becoming victims of our own sampling technique.

Sample Preparation

The laboratory generally receives a sealed jar of soil. The laboratory will commence preparation of the sample for analysis for your selected range of metals. However! — different laboratories prepare samples in different ways.

Some will dry the sample to remove moisture (if they didn't, the **number** you got wouldn't be the true **number**, it would be in mg kg^{-1} of wet soil, and how wet, exactly, is wet? Well that would vary from day to day, summer to winter, sand to peat).

Moisture content can really skew a sample result. Some labs will dry the sample before they analyse it. (Did they air dry it, or oven dry it? What happened to volatiles like mercury if they did?) Some will dry a fraction in parallel to the analysis and back-calculate the final result to the dry-weight of samples. (Did you give them enough sample to enable them to do that?) Others simply report results "as received".

So, then, if they dry it, how dry is dry? Totally moisture free? 5% moisture? 25% moisture?

Did your laboratory analyse even one stone from your sample? Probably not. They know you wouldn't appreciate that, so they probably *avoided* the stones (just as you did when taking the sample in the first place). In fact, most labs will grind your soil sample to pass through a sieve of a given size. This is done for two reasons: firstly to increase the overall surface area of the sample exposed to the extracting acid; and secondly to allow removal of unwanted or unrepresentative particles such as pieces of wood, vegetable roots and other sample 'contamination', so if your soil in the field has, say 25% fine gravel content, that gravel may also be removed prior to analysis, and if your soil was actually more of a gravel than a soil, goodness knows what proportion of the original field soil is finally analysed and how true a concentration the **number** might represent.

How many people specify 'moisture content' or 'stone content' as a parameter to their laboratory to enable them to accurately assess their **numbers**? Not many!

How many laboratories actually prepare your entire sample? Not many! Anyone who has ever re-called an analysed sample from a competent laboratory will find that there is an

undisturbed fraction of the original sample still in the jar, so the lab actually only worked with 50% or less of your sample. Well that's okay, because they are being professional, and keeping some in reserve in case you ask for further work to be done. How many have sent a 250-g sample to a lab and asked them to split that sample and forward a portion to a second lab? How much sample could each lab reasonably then have to work with? You should know. You sent it!

Analysis

What the hell, let's analyse it anyway. But how? Analytical techniques for metals have come a long way since the invention of the Atomic Absorption Spectrophotometer (AAS) by Australia's Alan Walsh in 1952. The modern descendent of the AAS is the Inductively Coupled Plasma Emission Spectrophotometer (ICP). Most (but by no means all) commercial laboratories now employ this latter technique, which can be incredibly sensitive to zinc… (but, sadly, not quite so sensitive to, say, mercury, selenium or tin). In order to avoid an overload of the system, a very small portion (fraction) of your sample, often less than 1 gram (just about enough to cover your fingernail) will be selected for analysis (which will reduce dramatically the potential for zinc 'calibration overload', …and reduce the ability to detect mercury, selenium and tin even further, as they will probably all be analysed from the same acid extract).

We are now typically dealing with one single gram of soil representing up to 500 m^3 of a potentially contaminated site. Minimum recommended sampling density for a 1 ha site according to AS4482.1.

Now, in order to analyse the (now stone-free) soil, most laboratories will extract the heavy metals (including zinc) into an acid solution … but which acid? Certain metals such as lead and tin do not dissolve terribly well in hydrochloric acid. Too much sulphuric acid may 'mask' some analytes in the ICP, so the acid choice is critical, but not all laboratories use the same acid mix.

And what about the extraction technique? Do they put the soil in a beaker on a hotplate in a fume cabinet and boil it? (What happens to volatile metals like mercury then?). If so, for how long, and at what temperature—the boiling temperature will clearly be a function of the selected acid mixture, as will the efficiency of the extraction? Some labs use microwave digestion systems instead of hotplates (like little pressure cookers inside an industrial microwave oven), but then the fraction analysed is even smaller, often 0.3g or less. To complicate matters even further, microwave digestion is often described on the basis of a power setting, (typically 800 - 1200W) for a set period of time, so a difference of only a few millilitres of acid between two digestion flasks might influence the efficiency of the extraction. Temperature is easy to measure in a beaker, but how does the lab know that the microwave is delivering the right Wattage? Won't the process be more aggressive if the microwave oven is only half-full? Some state of the art microwave digestion systems have temperature measurement devices, but not all vessels can be at the same temperature, and fine control is lost.

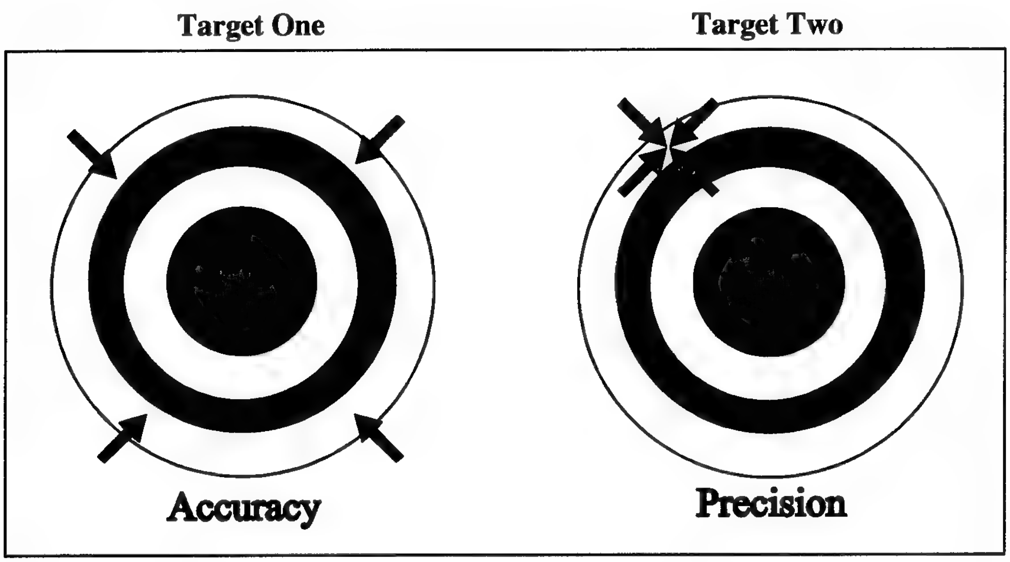
The efficiency of the extraction may also be dependent upon the soil type - soils with a substantial organic content not always being willing to give up their metals without additional oxidation with peroxide or similar.

Following digestion the acid extract will be filtered (to remove solids) made up to a known volume with de-ionised water and analysed by passing through the ICP, which has been calibrated using a series of standard solutions.

Solutions and Fading Lights

Ask the laboratory honestly what their recovery rates are and they will tell you that it varies from soil to soil, batch to batch, but is never 100%. (some *do* provide those data in their reports, but who ever actually *reads* it). Ask them what their degree of accuracy is, and what is the precision of the analysis, and that's generally a different story.

Studies carried out in the UK and Hong Kong have shown that the in-house reproducibility between different analysts in the same laboratory can often vary by plus or minus 20% at mg kg^{-1} level analysis. Variations between laboratories can reach factors of ten or more dependent upon the analyte and the sample matrix, and these interlaboratory tests utilise standard samples prepared especially for the study (the 'Contest' inter-laboratory sample exchange scheme). We, in Australia, seem to place a great deal of store in the RPD (relative percentage difference) between replicate analyses of the same sample, but this simplistic approach denies one of the great truths in chemical analysis; that accuracy and precision are not the same thing.



The four results in Target One above are accurate, for although no individual result is correct, and although they are fairly different from each other, on the average they hit the bulls-eye. The four results in Target Two are precise; they are all reproducible and in the same place, but not at all accurate in their reflection of the location of the bull.

So, in-house, laboratories can achieve an average precision variance of, say, $\pm$10%, multiplied by an accuracy variance of say $\pm$10%, but they cannot regularly achieve that between laboratories.

How can that be? These laboratories have been granted accreditation by NATA! Truth is that the accreditation is based around the general requirements of the ISO 9000 series of international quality standards. These were standards not designed for laboratories but for manufacturing industry. In short, they are standards which reflect more upon traceability of raw material and consistency of product than on the actual final outcome. For manufacturing, this could in theory mean that a company manufacturing dud light bulbs could obtain an ISO 9000 series accreditation for dud light bulb manufacturing providing every light bulb was properly manufactured and labelled, and every single one they ever produced was a dud. NATA, thankfully, is more circumspect and requires laboratories to demonstrate that their

methods have been validated and do actually work. However, the emphasis is still more on consistency, traceability of standard materials, calibrations and reproduceability of results than getting close to the 'right' result. This means that a NATA accreditation might be obtained for an analytical method which has a validated recovery of an analyte from a standard sample of only 80%. It is important to note, however, that 100% recovery of many analytes is just not possible with today's technology.

Commercial laboratories in Europe are now being pressed to report results which give degrees of accuracy, i.e. zinc 200 mg kg^{-1} $\pm 20\%$ (or, somewhere between 160 and 240). Sadly, for some analytes at certain concentrations this can present a problem. Try sending a client a result of 1 mg kg^{-1} $\pm 40\%$ for mercury then explaining exactly what that means in the real world.

Generally speaking, the lower the concentration, the lesser the accuracy which can be claimed for the **number.** Some have suggested that consultants have an unrealistic expectation of accuracy. Others have suggested that it is an unrealistic *requirement* for accuracy. To be practical, in a drinking water or groundwater sample an accuracy to around part-per million level or better is pretty much essential. For a contaminated soil, does 20 or 30 mg kg^{-1} variation in a zinc or lead result really matter to the final recommendation? In most cases probably not, except when that result is frighteningly close to a guideline, standard or limit!

There is no doubt that both accuracy and precision diminish with the reporting units. The ability to detect smaller and smaller quantities of a substance in a sample has not been accompanied by a proportional confidence in the accuracy or the precision of that result. A sample reported at 20% has a greater chance of being correct in terms of accuracy and precision than one of 20 mg kg^{-1}, and by the time we get to 20 μg kg^{-1} we are really stretching the bounds of trust. Hence the reason why laboratories quote low numbers in terms of limit of detection, i.e. a 'less-than' result. It has been suggested by some that as we move downwards in range from percent through part-per-million to part-per-billion levels the ink used by the laboratories should become progressively greyer to graphically reflect the accuracy level, until at part-per-trillion level we have white ink on a white parchment. Whilst such a blatant move would scare many, it is really no different to asking for a result which also expresses a confidence interval.

Betwixt and Between

We have all seen the differences in **numbers** reported by two laboratories on identical samples sent. *Why does it happen?* Because labs don't all do the same thing! They use different preparation methods (try sending a gravel sample to two different labs and see the differences in results). They use different extraction methods. They use different analytical methods. (At the last count there were about 63 separate published methods for analysis of mercury in soil.) They use different staff. They use different reporting protocols.

I would stress at this point that this is not the fault of the laboratories. They work within the confines that we, their clients, give them and cannot do work for which we, with our desire to depress costs, are not willing to pay. Bearing in mind the detailed work described above (admin, sample preparation, weighing, extraction, calibration, analysis, reporting and profit margin) and adding the overhead cost of good laboratory instruments at several hundred thousand dollars each, and the fact that we now demand rapid turnaround times often of 48 hours or less, what degree of accuracy do we expect for $3.00 per analyte?

THE CONSULTANTS' REPORT

To re-cap: You stand before the judge. Based upon less than one fingernail of sample, removed from a jar of soil selectively taken from a site somewhere, prepared in a manner you don't know; and analysed by a method whose intricacies and uncertainties you don't understand you may have received a **number.** The accuracy of that **number** is not certain, and it is reported to a protocol which may add bias. You have compared your **number** to somebody else's **number,** (ANZECC B, NEHF, Dutch, USEPA), without knowing how that was derived either, yet you write a conclusion, prepare a recommendation, and bill your client.

So now we come to the big question. Which method did ***your*** lab use? It is clearly essential to understand how your lab derived the **number** for only then can you properly assess it. There are no *right* methods (albeit that there are plenty of wrong ones). Remember that your chosen laboratory has received a NATA certification for their analytical method, and if you instruct the lab to change that method, their accreditation no longer applies, and it is that very accreditation that you will use to justify your conclusions based upon their results. Your only means of assessing that **number** is to accept the sampling protocol and analytical method that were used to derive it, but to understand the particular influence or skew that the method might have introduced to the sample result and then use your professional judgement to supply an interpretation which accounts for any bias. If that means back-calculating to allow for moisture or stone content, or for possible vapour losses or sulphate ion masking in the ICP, then so be it. At least you will be able to stand before that man with the wig and the gown and tell him you **do** understand.

Okay, having seen the variability which can be introduced to the reported **number** by sampling and analytical method selection, which methods did ANZECC or the Dutch use? What? ...They didn't say? Tell that to the judge!

CONCLUSIONS

Analytical laboratories, unlike photographic laboratories, are not a one-stop shop where you drop off your samples or films today and pick up your perfectly processed results tomorrow. Every sample is different. Civil engineers already know that sands behave differently to clays, behave differently to loams and peats yet are often too naive to realise that same principle applies equally to the way they behave under analytical extraction. Do we understand the differences, or fund laboratory analysis sufficiently to allow differentiation in extraction technique? Sadly, seldom.

The ideal extraction and analysis techniques for arsenic, mercury and tin differ from those for copper nickel and zinc, yet we never question which was used, or offer an extra few dollars to get the best option.

By our insistence upon ever lower costs and ever faster turnarounds we have, by our own actions, changed laboratories from institutions of scientific excellence to low-cost result production lines. We have changed Louis Pasteur's dream of "Temples of the future" into scientific fast-food restaurants. We then blindly accept this production line's numerical output and, with a faith seldom seen outside of organised religion, pass these forward to our clients as Gospel, seldom, if ever, questioning the validity or derivation of those **numbers.**

Talk to your laboratories; listen to what they say; ask their advice; understand what they do and why they do it. Then, and only then, can you sign that report and have pride in the conclusions you so righteously penned and faith in the recommendations that will dictate the cost, and effectiveness of any remedial actions that flow from them.

The Enhanced Remediation Strategy at the Homebush Bay Olympic Site

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ABSTRACT: The site of the 2000 Sydney Olympic Games at Homebush Bay was previously a highly degraded site experiencing industrial activities, landform modification and waste dumping. Winning the Olympic Games provided the impetus and funding to consolidate the waste and remediate the site. Monitoring was put in place to meet licensing requirements and observe impacts from specific activities, like construction. However, the NSW Government also put aside funds for the enhanced remediation strategy, to determine the condition of the site as a whole, report data in a easily used format and make recommendations for the long term management of the site after the Games.

KEYWORDS: landfill, remediation, triad monitoring, bioremediation, GIS

INTRODUCTION

Since World War II over 9 million cubic metres of domestic, commercial and industrial waste have been dumped at the Homebush Bay Olympic site. The landscape has been dramatically modified by concreting water channels, reclaiming land and removing native vegetation. Prior to the initiation of remediation works in 1995, aerial photos and monitoring results show a highly degraded environment with a variable waste matrix across the site.

Prior to remediation, monitoring data generated by various bodies over the past twenty years indicated significant degradation in sediment and water quality and detrimental impacts on various species of fauna and flora, as well as an erratic chemical concentration level in soils and water. Remediation was based on the need to improve surface water quality by removing the exposure pathways from waste dumps to the wetlands and waterways. After discussion with stakeholders, the OCA decided waste management on-site was preferable to exporting the waste and contaminated soil elsewhere. Waste was consolidated into discrete areas and a *wet landfill* approach (e.g. Fig. 1) was adopted to ensure that leachate was captured prior to migration to the environment. Surface stormwater paths were redirected around contaminated land and cut-off walls were inserted to protect the waterways where necessary.

Now that most remediation work has been completed at the site, a visual inspection and chemical monitoring program of the leachate system has been implemented this year, as specified by NSW EPA licence requirements.

As part of the Enhanced Remediation Strategy (ERS), an initiative funded by the NSW Government that focuses on securing an environmental legacy from the Sydney Olympic Games, a more complete monitoring program that examines the site as a whole has been implemented.

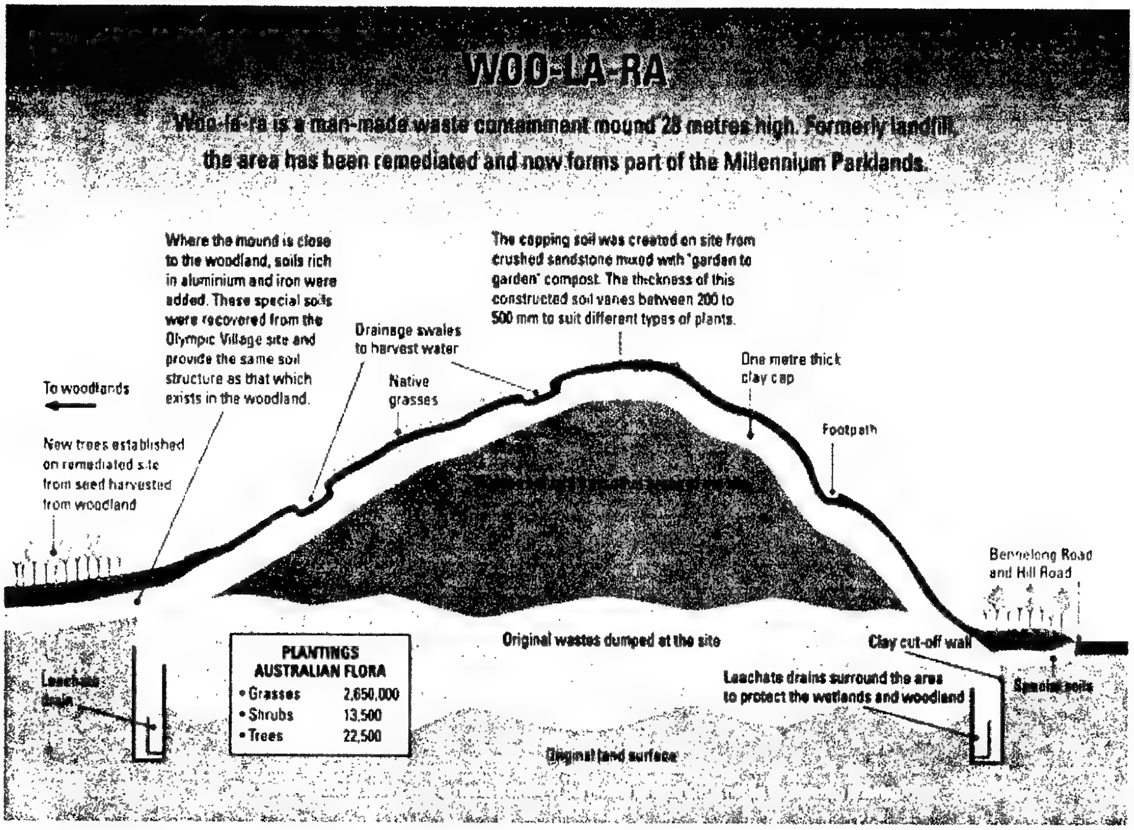

Fig. 1. Example of on-site waste containment

METHODS

The Ecology Programs has been set up to implement the ERS. The program has 3 distinct projects; the Ecology Databank, which presents data in a user friendly format using a Geographic Information System (GIS) base; the Biological Monitoring project, which aims to determine the condition of the site and base long term management recommendations on the data collected; and an Education Program, which will provide tools to present information to the community.

The Biological Monitoring program has a number of objectives. By compiling data collected over the past 10 years and making judgements on the quality of this data, a judgement on the condition of the site and changes over time may be made. The compilation and interpretation of this data goes beyond meeting discharge or contaminated site licences. Data is collected by location as a result of dividing the site into sub-catchments. The information is easily loaded into the GIS and allows for the identification of monitoring gaps. Indicators to monitor condition were selected if they were applicable to a large number of previous studies and were judged as relevant to determining state of health. Extra monitoring has also been implemented site wide, with testing based on a variety of environmental situations, from determining sediment quality in estuarine wetlands to leachate trapping systems. Toxicity testing was included for the first time to give information on bioavailability and impacts from a mixture of chemicals.

Toxicity testing together with chemical and biota monitoring forms a 'Triad Testing' process, which will provide a weight-of-evidence approach to determine the condition of the site and provide a useful baseline for future monitoring. Although discharge licences specify final chemical concentrations to be met before releasing wastes, leachate enclosed in a system

requires further monitoring to understand possible impacts. The triad monitoring is a state of the art approach, which has advantages over chemical or biological monitoring on their own. It provides a weight-of-evidence method that provides extra confidence in results observed. This enhanced monitoring contributes to effective contingency plans being put in place (based on real potential impacts and an understanding of possible effects) in case of system failure, and the likely impacts if leachate is re-used.

Also included in the Biological Monitoring testing regime is a bioaccumulation study on fish in site wetlands, and a project confirming enhanced bioremediation of BTEX and PAHs is occurring due to indigenous microorganisms.

All project experimental design and results will be reviewed by a panel of independent experts and then entered into the Ecology Databank. The Databank is designed as a user-friendly tool for long-term management. The search and retrieval structure will be browser based so information can be easily obtained without requiring specialised software or further training.

RESULTS

A baseline level of toxicity, chemical and biological indicators is being set which will allow a determination of recovery of the environment over time. Trends in the indicator levels will also be assessed to determine if any changes can be established so far and what actions may need to be implemented.

The triad monitoring regime has initially been established for those sites with potential exposure pathways, starting with soil and sediment. Should the sediment tests show any adverse response, pore water and surface waters may be recommended for further testing. Initial results for soil contamination at Wilson Park indicate no toxicity in the bio remediated topsoil or in elutriates. There is, however, remaining contamination in the groundwater (which is being treated in evaporation ponds) and pond sediment. Results from sediment analysis are still being assessed.

Responses in the evaporation pond water appear to be due to hydrocarbon contamination. These responses should be significantly reduced in the future due to biofiltration mats containing indigenous BTEX degrading microorganisms being placed in the pond and optimal conditions for their growth being maintained. Our first recommendation of monitoring these ponds at a number of locations, not just at final discharge points, is being assessed by OCA management.

DISCUSSION

This pilot work will provide information for determining what long term monitoring may be required in the future. We believe this approach provides a more holistic understanding of the site that goes beyond the legal requirements for monitoring. We hope that by obtaining adequate base information, we can conduct monitoring in the future that is based on an understanding of what processes are occurring at the site.

Author Index

Keyword Index